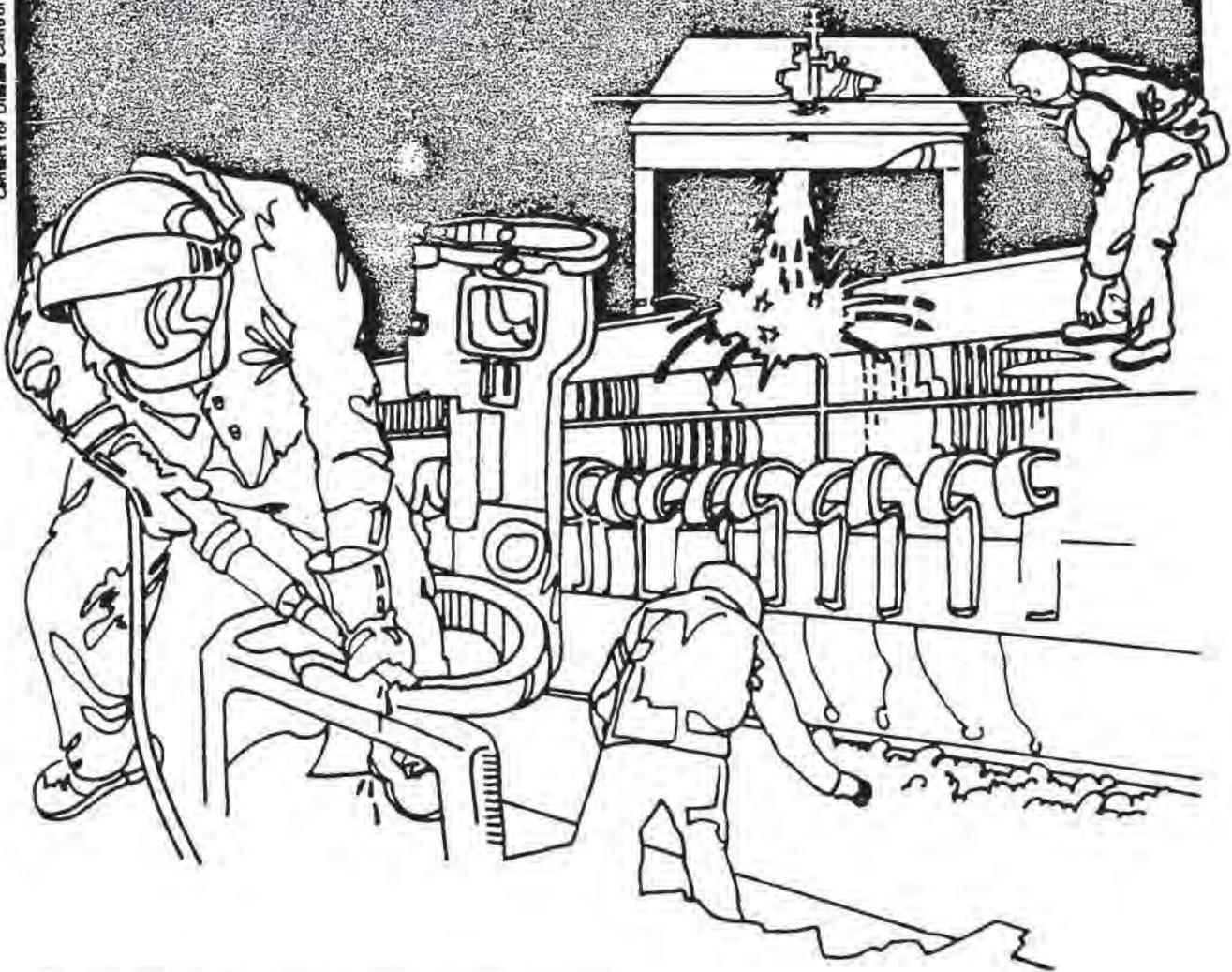


# NIOSH



## Health Hazard Evaluation Report

HETA 82-292-1358  
SEA ROAD CONSTRUCTION  
STATE OF WISCONSIN

## 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, medical, nursing, and industrial hygiene technical and consultative assistance (TA) 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.

## I. SUMMARY

On June 14, 1982, the National Institute for Occupational Safety and Health (NIOSH) received a request to evaluate occupational exposures during sulfur extended asphalt (SEA) road construction in the State of Wisconsin. The requestor was concerned with reported incidents of nosebleeds, chapped and split lips, severe sunburn, and extreme nausea and vomiting among employees working on SEA paving projects.

In June 1982, NIOSH investigators conducted an initial survey of a SEA resurfacing operation. Air samples were collected for qualitative characterization of process emissions. In September 1982, follow-up environmental surveys were conducted at additional SEA projects. Personal breathing zone and area air samples were collected, operational and environmental factors were monitored, and interviews were conducted with employees.

Personal breathing zone and area air samples showed time weighted average (TWA) concentrations of total particulate ranging from 0.5 to 5.6 milligrams per cubic meter of air ( $\text{mg}/\text{M}^3$ ), with a mean of 3.1  $\text{mg}/\text{M}^3$ . TWA concentrations of respirable particulate ranged from 0.2 to 5.1  $\text{mg}/\text{M}^3$ , with a mean of 2.4  $\text{mg}/\text{M}^3$ . Elemental sulfur, comprising approximately 100% of the particulate matter collected, was determined to be the primary component of the SEA emissions. No standard presently exists for sulfur dusts or fume.

Fifteen-minute TWA concentrations of hydrogen sulfide ranged from below the limit of detection of 1 part of contaminant per million parts of air (ppm) to 6 ppm, with instantaneous concentrations ranging as high as 10 ppm. All samples were below the NIOSH recommended standard of 10 ppm for a ten minute period and below the current OSHA standard of 20 ppm. TWA concentrations of sulfur dioxide ranged from 0.01 to 0.04 ppm, with a mean of 0.02 ppm. No sulfur containing organic compounds were detected in the emissions.

Essentially all of the employees at the SEA paving sites reported some degree of eye irritation, and to a lesser extent upper respiratory irritation. The degree of irritation was dependent on the proximity to the paver where the emissions were highest. Because the employees interviewed lacked experience with SEA paving (average 2 - 4 days), potential health effects from longer-term exposure could not be assessed.

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On the basis of the data obtained during this investigation, NIOSH has determined that a potential hazard of eye and mucous membrane irritation existed during the SEA paving operations evaluated in these surveys. Although contaminant concentrations were below the corresponding environmental criteria, irritative effects attributable to the emissions were still experienced by the employees. Recommendations designed to alleviate this hazard are included in the full body of this report.

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## II. INTRODUCTION

On June 14, 1982, a representative of the Wisconsin Operating Engineers requested a NIOSH health hazard evaluation of sulfur extended asphalt (SEA) road paving projects being conducted under contract for the Wisconsin Department of Transportation (DOT). The requestor was concerned with employee complaints of frequent nosebleeds, chapped and split lips, severe sunburn, and extreme nausea and vomiting resulting from asphalt paving projects where sulfur was being added to the asphalt binder.

On June 24, 1982, NIOSH investigators conducted an initial survey of a SEA resurfacing operation on Wisconsin State Highway 13, northwest of Racine, WI. Background information related to the process was obtained, and air samples were collected for qualitative characterization of process emissions. The preliminary results of this survey were transmitted by letter to the requestor and the Wisconsin DOT on June 30, 1982.

Following the initial survey, NIOSH investigators conducted environmental surveys at two SEA paving sites; on September 2, 1982 at a project on State Highway 14, east of Janesville, WI, and on September 14 and 15, 1982 on a project on State Highways 14 & 61, southeast of La Crosse, WI. During these surveys, personal and area air samples were collected, operational and environmental factors were monitored, and interviews were conducted with employees working on the paving crews. The results of these surveys were transmitted by letters to the requestor and the Wisconsin DOT on October 5, 1982 and March 5, 1983.

## III. BACKGROUND

### A. Asphalt Paving

Asphaltic concrete may be generally defined as an intimate mixture of coarse aggregate, fine aggregate, and asphalt cement. The mixture is usually hot mixed at a central mixing plant and hot laid to form pavement. The process is generally performed by first feeding the aggregate into one end of a drier (a large rotating cylinder mounted at an angle with the horizontal), where the aggregate is heated to temperatures ranging from 250 to 350°F, and then discharged into a mixer (pugmill) simultaneously with a binder material (normally asphalt) which has been preheated to 225 to 325°F. Mixing is continued for a fixed length of time and the mixture is then discharged into a silo for subsequent loading into trucks, which are covered with tarpaulin to maintain temperature, and transported to the paving site.

At the paving site the trucks dump the asphaltic concrete mixture into the receiving hopper of a bituminous paver which combines the functions of spreading and finishing in one machine. The material is fed from the hopper toward the finishing section on the paver and is generally spread and agitated by means of screws or other agitator-distributors which insure uniform spread of the mixture and loosen the material. The spread material is then struck off at the desired elevation and cross

section by one or more screeds. The screeds are usually provided with heating units to prevent pick-up of the material during the spreading and finishing operations.

Compaction is generally accomplished in two stages. A "hot" roller operates directly behind the paver, while the mixture is still hot (250°F or hotter), and makes one pass over the freshly laid pavement (overlapping about one half of the roller width). A second roller trails the paving operation at some distance and continues rolling until all roller marks have been eliminated and a high degree of compaction of the mixture has been secured, in order to provide high density and stability of the pavement.

#### B. Use of Sulfur in Asphalt Paving

Considerable research has taken place since the mid-1960's examining the potential use of elemental sulfur in asphalt paving operations.<sup>1</sup> Much of this interest has been a result of the concern with the rising cost and availability of crude petroleum, from which asphalt is derived. In addition, sulfur is one of the few elements which is predicted to be in abundance over the next several decades. This is in part due to the increasing amount of secondary sulfur obtained as a result of pollution abatement controls for power plant emissions. The amount of reclaimed sulfur is anticipated to increase further following commercialization of several new energy processes; shale oil, coal liquification, synthetic natural gas, etc.<sup>2</sup> Additionally, claims of enhanced qualities when sulfur is introduced in asphalt mixtures has also generated considerable interest in these processes. These claims include: increased strength, lower viscosity, lower mixing temperatures, improved stress fatigue characteristics, and resistance to gasoline, diesel fuel, and other solvents.<sup>1</sup>

There are three primary types of sulfur asphalt mixtures currently in various stages of testing and usage. The first is a Sand Asphalt Sulfur Mixture (SAS), and is composed of a hot-mix of sand, asphalt and sulfur. Because of the binding properties of the sulfur, poorly graded sand can be used in situations where suitable aggregate is not available. A second material being examined is referred to as Plasticized Sulfur, in which sulfur and polymeric sulfide additives completely replace asphalt in the paving mixture. The third type of mixture, and the one which was examined in this survey, is referred to as Sulfur Extended Asphalt (SEA), Sulfur Asphalt Binder Mix (S/A), and sulfur/asphalt emulsion. In this process sulfur and asphalt both act as the binders. Varying amounts of the two binders have been used in this type of system, with the percentage of sulfur to asphalt in the mixture ranging from 30/70 to 50/50.

#### C. SEA Paving Operations in Wisconsin

The Wisconsin DOT specified SEA mixes for use in several road paving projects between 1981 and 1983. In anticipation of future trends, the intent was to gain familiarity with the handling and application of the material and to test the characteristics of SEA road surfaces under Wisconsin road use and climate conditions.

Two major types of SEA mixes are used in paving projects contracted by the Wisconsin DOT. The first is a "virgin mix", in which the binder is composed of 30% sulfur/70% asphalt by weight. Since the binder composes only 5-6% of the final mix (aggregate being the primary constituent), the amount of sulfur in the final mix is 1.8%. The second type of mixture being utilized is referred to as "recycle mix". In this process, old asphalt surfaces are removed, milled, and readded to the new asphalt mixture at a ratio of 60 to 70% old material and 30 to 40% new material (aggregate). Utilizing the same sulfur/asphalt binder ratio for the new aggregate as the virgin mix, approximately 0.59% sulfur will be present in the final "recycle mix".

SEA road paving operations are conducted in essentially the same manner as the traditional asphalt paving operations described in subsection A. Some additional equipment is necessary for handling the sulfur in the molten stage (the melting point of sulfur is approximately 240°F). Molten sulfur is delivered to the batch plant site in heated tank trucks. The sulfur is then transferred to a specially designed tank which keeps the sulfur in the molten state for introduction into the mixer along with the heated asphalt.

During all paving projects monitored, an operator was responsible for maintaining the controls of the paver. During paving, a screed operator follows alongside the paver to make adjustments on the screed and to ensure that the asphalt is being properly distributed on the road surface. Additionally, one or two laborers follow the paver to fill in irregularities in the pavement surface. One operator follows in close proximity on the "hot" roller which packs the SEA before the temperature drops below approximately 250°F and before the sulfur solidifies, and a second roller operator trails the paving operation, completing the compaction process. The distances the rollers operate behind the paver may vary greatly due to mix temperature, ambient temperature, and a number of other factors.

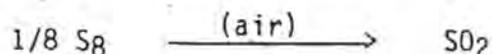
A variety of different types of respirators and eye protection were available to the employees at the paving sites. Use of this equipment was usually left to the discretion of the individual employee.

#### IV. METHODS AND MATERIALS

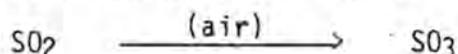
##### A. Potential SEA Emissions

Prior to the environmental surveys, a review of the literature was conducted to obtain the results of previous studies of SEA paving operations. Several studies were identified, including work conducted by the Bureau of Mines, the Sulfur Institute, and the Federal Highway Administration. The most comprehensive study noted in the literature had been conducted by the Texas Transportation Institute under contract by the Federal Highway Administration.<sup>2</sup> This study provided a discussion of possible reactions which could occur during SEA mixing and paving operations. In order to provide a clearer understanding of the rationale for the sampling methodology utilized in this evaluation, the following summary of these reactions is presented.

Since S/A mixes are heated to temperatures between 265° to 300° F, there is a potential for the evolution of both gaseous and particulate emissions. One such reaction, the oxidation of elemental sulfur (S) to sulfur dioxide (SO<sub>2</sub>) gas, is possible as indicated by the following reaction:

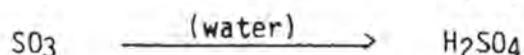
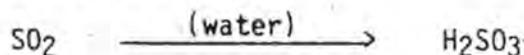


This in turn can be oxidized to form sulfur trioxide (SO<sub>3</sub>) as follows:



however, this reaction is reported to proceed slowly in the absence of a catalyst.

Since both SO<sub>2</sub> and SO<sub>3</sub> are soluble in water, it is possible for them to form their respective acids, sulfurous acid (H<sub>2</sub>SO<sub>3</sub>) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), in the presence of water vapor or high humidity as shown in the following reactions:



Sulfur also may react with many different organic compounds to yield a variety of reaction products. The reaction of sulfur with one hydrocarbon group, the olefins (RCH<sub>2</sub>-CH<sub>2</sub>R'), can result in the dehydrogenation of the carbon atom (R) and the formation of hydrogen sulfide (H<sub>2</sub>S) in the following manner:



Hydrogen sulfide can also be generated by the reaction of sulfur with two separate hydrocarbon compounds (2RH) which can result in either the coupling of the two hydrocarbons or the formation of an organic sulfide. Both reactions can result in the production of H<sub>2</sub>S as demonstrated by the following reactions:



The reaction products resulting from the combination of sulfur and organic constituents of asphalt are very complex and have not been fully detailed as of yet. However, these organic compounds would be expected to be relatively nonvolatile at the temperatures normally encountered in the SEA mixing and paving process.

In addition to the gaseous emissions occurring, sulfur may also be given off as a particulate, where it will either remain in this form until it is deposited or it may be slowly oxidized.

#### B. Survey Design

An initial survey was conducted by NIOSH investigators on June 24, 1982 at a virgin SEA resurfacing operation on State Highway 31, west of

Racine, WI. Background information related to the paving process was obtained and general area air samples for characterization of process emissions were collected. Direct reading short and long-term detector tubes were utilized in order to detect the presence of hydrogen sulfide and sulfur dioxide (Dräger®; SO<sub>2</sub> 5/a-L, H<sub>2</sub>S 1/c, 5/a-L and MSA® SO<sub>2</sub>). Additionally, sampling pumps were utilized at a flow rate of 1.0 liters per minute (Lpm) attached with Tygon® tubing to either a charcoal tube or membrane filter collection media. Charcoal tubes were used to collect gaseous emissions for 10, 30, and 97 minute sampling periods. A mixed cellulose membrane filter was used to collect particulate emissions for a 97 minute sampling period. All samples were "process samples" collected approximately 12 inches above the screed where high contaminant concentrations would be expected. The charcoal tubes were analyzed using a microwave plasma emission spectrometer/gas chromatography system for organosulfur compounds, and the membrane filters were analyzed by X-ray fluorescence spectrometry (XRF) for the presence of 74 elements above fluorine.

In order to quantify personal exposures to SEA emissions during paving operations, follow-up surveys were conducted by NIOSH investigators at two paving sites; on September 2, 1982 on a recycle mix project on State Highway 14, east of Janesville, WI, and on September 14 and 15, 1982 on a virgin mix project on State Highways 14 & 61, southeast of La Crosse, WI. During these surveys, personal samples were collected, when possible, near the breathing zone of the employees. When the collection of personal samples was not possible (as with the equipment operators), area samples were collected as close to the employee as possible in order to reflect approximate breathing zone concentrations. The number of samples, collection media, flow rates, and method of analysis were as follows:

- a) Twelve pre-weighed 37 mm polyvinylchloride (PVC) membrane filters collected at 1.5 Lpm and analyzed by gravimetric analysis for total particulate weight, and by XRF for sulfur content.
- b) Seven pre-weighed 37 mm PVC filters collected using a 10 mm nylon cyclone sampled at 1.7 Lpm and analyzed by gravimetric analysis for respirable particulate weight, and by XRF for sulfur content.
- c) Nine 37 mm MCE filters followed in line by 37 mm filters impregnated with potassium hydroxide collected at 1.5 Lpm analyzed by NIOSH method P&CAM 268 for particulate sulfates and sulfites, and sulfur dioxide.<sup>3</sup>
- d) Nine long-term Draeger® detector tubes (H<sub>2</sub>S 5/a-L) collected at 20 cc/min were analyzed by direct reading of colorimetric reaction for hydrogen sulfide.
- e) Five long-term Draeger® detector tubes (SO<sub>2</sub> 5/a-L) collected at 20 cc/min were analyzed by direct reading of colorimetric reaction for sulfur dioxide.
- f) Six MDA Monitox® Model 4100 mini-dosimeter samplers equipped with H<sub>2</sub>S detectors providing direct readout, continuous 15 minute TWA's, and integrated TWA's for the duration of sampling.

The duration, location, and other information pertinent to sample collection is included in Tables 1 through 5.

During these surveys, various environmental and operational parameters were periodically measured to determine any influence which they might have on emission levels. These included; wind speed and direction, relative humidity, ambient air temperature, and asphalt temperature.

#### V. EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects if their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy).

In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the evaluation criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: 1) NIOSH Criteria Documents and recommendations, 2) the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLV's), and 3) the U.S. Department of Labor (OSHA) occupational health standards.<sup>4,5,6</sup> Often, the NIOSH recommendations and ACGIH TLV's are lower than the corresponding OSHA standards. Both NIOSH recommendations and ACGIH TLV's usually are based on more recent information than are the OSHA standards. The OSHA standards also may be required to take into account the feasibility of controlling exposures in various industries where the agents are used; the NIOSH-recommended standards, by contrast, are based solely on concerns relating to the prevention of occupational disease. In evaluating the exposure levels and the recommendations for reducing these levels found in this report, it should be noted that industry is legally required to meet only those levels specified by an OSHA standard.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8- to 10-hour workday. Some substances have recommended short-term exposure limits or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from high short-term exposures.

The environmental criteria, along with a summary of the toxicological properties of the major substances encountered in this evaluation are presented as follows.

#### A. Sulfur

Sulfur is one of the most widely used raw materials in the chemical industry, and is utilized in the manufacture of pesticides, fertilizers, and a variety of other products. The dust of sulfur is capable of irritating the eyes. Different forms of sulfur dust have been noted to cause slight to severe eye irritation. The threshold for ocular irritation of sulfur in an aerosol form has been reported to be 0.2 ppm for the amorphous form, and 9 ppm for the crystalline form. Sulfur dust has been noted in the literature to cause a delayed type of eye irritation.<sup>8</sup> An individual may be exposed to sulfur dust for several hours, or even days, before developing a sensation of scratchy discomfort in the eyes, which may progress to burning or tearing, with blurring of vision. Complete recovery from these effects usually will occur within two or three days after exposure is discontinued. Symptomatology accompanying this form of irritation is very similar to that of hydrogen sulfide, and it is possible that the conversion of sulfur to hydrogen sulfide is involved, although this has not been completely investigated.<sup>8</sup>

Sulfur may also irritate the mucous membranes of the respiratory tract; however, there is no evidence that systemic poisoning results from the inhalation of sulfur dust. In one study, X-ray examination of workers exposed to appreciable amounts of sulfur dust for a seven year period showed no lung lesions which were attributable to inhalation of sulfur dust.<sup>7</sup> Currently, no environmental criteria exists specifically for sulfur dust or fume.

#### B. "Nuisance" Particulates

In contrast to fibrogenic dusts which cause scar tissue to be formed in lungs when inhaled in excessive amounts, so-called "nuisance" dusts are stated to have little adverse effect on lungs and do not produce significant organic disease or toxic effect when exposures are kept under reasonable control. The nuisance dusts have also been called (biologically) "inert" dusts, but the latter term is inappropriate to the extent that there is no dust which does not evoke some cellular response in the lung when inhaled in sufficient amount. However, the lung-tissue reaction caused by inhalation of nuisance dusts has the following characteristics: (1) The architecture of the air spaces remains intact; (2) Collagen (scar tissue) is not formed to a significant extent; and (3) The tissue reaction is potentially reversible.<sup>9</sup>

Excessive concentrations of nuisance dusts in the workroom air may seriously reduce visibility, may cause unpleasant deposits in the eyes, ears and nasal passages, or cause injury to the skin or mucous membranes by chemical or mechanical action per se, or by the rigorous skin cleansing procedures necessary for their removal.<sup>9</sup> The current OSHA standard for nuisance particulates is 15 milligrams per cubic meter of

air ( $\text{mg}/\text{M}^3$ ) as total dust, and  $5 \text{ mg}/\text{M}^3$  as respirable dust as an 8-hour TWA. ACGIH recommends a TLV of  $10 \text{ mg}/\text{M}^3$  for total dust.

#### C. Hydrogen Sulfide

Hydrogen sulfide ( $\text{H}_2\text{S}$ ) is a flammable colorless gas which is capable of accumulating in low lying areas, since it is heavier than air. Although it exhibits a characteristic rotten-egg odor at low concentrations, its ability to cause olfactory paralysis and the congenital inability of some persons to smell  $\text{H}_2\text{S}$  make odor a poor warning property.<sup>10</sup>  $\text{H}_2\text{S}$  may cause headache, dizziness, upset stomach, and irritation to the eyes and respiratory tract at low concentrations.<sup>6</sup> At high concentrations it can rapidly cause respiratory paralysis and asphyxia.<sup>11</sup> Exposures to 50 ppm for one hour can cause acute conjunctivitis, with pain and tearing. Often times, the onset of eye irritation associated with exposure to low level hydrogen sulfide may be delayed for several hours or days following exposure. In industries where the concentration is regularly kept below 10 ppm, it is rare to have any eye irritation.<sup>8</sup> The current OSHA standard is 20 parts of contaminant per million parts of air (ppm) or a maximum allowable peak of 50 ppm for 10 minutes once, if no other measurable exposure occurs. NIOSH has recommended that the permissible exposure limit be reduced to 10 ppm for any ten minute period.<sup>12</sup>

#### D. Sulfur Dioxide

Sulfur dioxide ( $\text{SO}_2$ ) is a colorless gas with a strong pungent odor. It is a severe irritant of the eyes and upper respiratory tract. Chronic exposure can cause rhinitis (runny nose), dryness of the throat, fatigue, inflammation of sinus passages, cough, and shortness of breath.<sup>10</sup> Sulfur dioxide rapidly forms sulfurous acid on contact with mucous membranes. This accounts for its severe irritant effects. In combination with certain particulate matter and/or oxidants, the effects may be markedly increased. In one study, workers repeatedly exposed to 10 ppm concentrations of  $\text{SO}_2$  experienced upper respiratory irritation and some nosebleeds, but the symptoms did not occur at 5 ppm.<sup>7</sup> It is estimated that 10 to 20% of the young, healthy adult population is hypersensitive to the effects of  $\text{SO}_2$  exposure. Recent studies have shown some chronic effects, such as chronic bronchitis and reduced pulmonary function at chronic exposures below the current federal (OSHA) standard of 5 ppm as an 8-hour TWA. NIOSH has recommended lowering the current standard to 0.5 ppm.<sup>13</sup>

#### E. Asphalt

Asphalt is a mixture of hydrocarbons which results from the distillation of the lighter hydrocarbons from petroleum, with partial oxidation of the residue.<sup>9</sup> The major effects from exposure to asphalt fumes are irritation of the eyes and the respiratory tract. Although asphalt contains small amounts of polynuclear aromatic hydrocarbons (PAH's), available information is insufficient to present a conclusion as to the potential carcinogenicity of asphalt fumes.<sup>14</sup> However, it is generally known that the oxidation of PAH'S destroys their carcinogenic

potential.<sup>9</sup> The differing character of the PAH fraction of petroleum asphalt fumes and those of coal tar pitch volatiles indicates less carcinogenic risk. Additionally, levels of one PAH (Benzo-a-pyrene) were noted in two studies to be approximately 0.03 percent of the amount normally found in coke oven emissions.<sup>15</sup>

Skin contact with hot asphalt can produce thermal burns and some photosensitization. In animals there is some evidence that asphalt left on the skin for long periods of time may result in local carcinomas, but there have been no reports of such effects on human skin that can be attributed to asphalt alone.<sup>14</sup> Although one reference source reported that sulfur and sulfur dioxide may act as stimulators of the effect of PAH's and other carcinogens for mouse skin, no specific studies were found which related this effect to asphalt.<sup>16</sup>

Because of the presence of minute quantities of cancer causing agents in some asphalts, NIOSH believes that asphalt fumes should be considered to be somewhat more hazardous than a nuisance dust. Therefore, an exposure limit of 5 mg/M<sup>3</sup> as determined by a 15 minute sampling period is recommended for asphalt fumes.<sup>14</sup>

## VI. RESULTS AND DISCUSSION

### A. Environmental

#### 1. Initial Survey Results

Long and short term detector tube samples collected during the initial survey did not reveal the presence of detectable levels of sulfur dioxide, and only trace levels of hydrogen sulfide. Analysis of the charcoal tube samples did not reveal the presence of any sulfur containing organic compounds. Analysis of the membrane filter sample revealed the composition of the dust collected to be almost entirely sulfur, with no significant quantities of any other elements detected.

#### 2. Follow-up Environmental Survey Results

Personal breathing zone and area air samples collected for total particulate revealed TWA concentrations ranging from 0.5 to 5.6 mg/M<sup>3</sup>, with a mean of 3.1 mg/M<sup>3</sup>. With two exceptions, all samples contained approximately 100% sulfur. When broken down by job, the highest average concentration was present at the paver (4.6 mg/M<sup>3</sup>) followed by the screed operator (4.5 mg/M<sup>3</sup>), the laborers (3.0 mg/M<sup>3</sup>), and the hot roller (1.1 mg/M<sup>3</sup>). No standard currently exists for sulfur dust. All samples were below the ACGIH recommended TLV for nuisance particulate of 10 mg/M<sup>3</sup> and the OSHA standard of 15 mg/M<sup>3</sup>. A complete listing of these results is presented in Table 1.

The results of the personal breathing zone and area air samples collected for respirable particulate revealed TWA concentrations ranging from 0.2 to 5.1 mg/M<sup>3</sup>, with a mean of 2.4 mg/M<sup>3</sup>. All samples contained approximately 100% sulfur. The average concentration was found to be highest for the paver (4.2 mg/M<sup>3</sup>), followed by the hot roller (0.6 mg/M<sup>3</sup>). Although no standard currently exists for respirable sulfur dust, one area sample was above the OSHA standard for

respirable dust of 5.0 mg/M<sup>3</sup>. A complete listing of these results is presented in Table 2.

The results of area samples collected for particulate sulfate and sulfite revealed TWA concentrations of sulfates ranging from 0.01 to 0.02 mg/M<sup>3</sup>. No sulfites were detected in these samples. Currently, no occupational standards exist for exposure to airborne particulate sulfates or sulfites. A complete listing of these results is presented in Table 3.

The results of area samples collected for hydrogen sulfide revealed 15-minute TWA concentrations ranging from below the limit of detection of 1 ppm at the hot roller to 6 ppm at the paver. Instantaneous concentrations of H<sub>2</sub>S noted on the direct reading sampling device ranged as high as 10 ppm. Results of the long-term detector tube samples revealed trace concentrations of H<sub>2</sub>S, but were below the limit of quantitation. All samples were below the NIOSH recommended standard of 10 ppm for a ten minute period and the current OSHA standard of 20 ppm. A summary of these results is provided in Table 4.

The results of the personal and area samples for sulfur dioxide revealed TWA concentrations ranging from 0.01 to 0.04 ppm, with a mean of 0.02 ppm. The average concentration was found to be highest for the laborer (0.04 ppm) followed by the paver (0.03 ppm), the screed operator (0.02 ppm), and the hot roller (0.01 ppm). Concentrations of SO<sub>2</sub> were below the limit of detection of 1 ppm in all long-term detector tube samples collected. All samples were below the NIOSH recommended standard of 0.5 ppm as an 8-hour TWA and the current OSHA standard of 5 ppm. A complete listing of these results is provided in Table 5.

### 3. Comparison of Side-by-Side Sample Results

Table 6 provides a listing of samples which were collected side-by-side for the same sampling period. Results of the particulate sampling reveal the composition of the dust to be almost entirely sulfur in most samples. The two samples which indicated the lesser percentages of sulfur were collected on a day in which gusting winds may have caused blowing of particulate material from nearby fields and the roadbed and subsequent collection on the filter media. Although the dust was determined to be almost totally sulfur, total particulate sulfate and sulfite were found only in extremely small quantities (average 0.3% of total dust). Comparison of the total and respirable dust fractions indicates that on the average, the respirable fraction comprised approximately 84% of the total dust collected. This data therefore indicates that elemental sulfur fume is the major constituent of the particulate emissions from the SEA mixture.

### 4. Comparison of Sample Results with Environmental and Operational Parameters

Table 7 provides a daily average of the wind speed and direction, the direction of paving operations, the wet and dry bulb air temperatures, the relative humidity, and the asphalt temperature. Due to the daily variability of a number of factors, no definite conclusions can be drawn when compared with the environmental results. However, visual

observations and limited direct reading and short-term results indicated that the wind speed and direction were important factors in influencing emissions in these surveys. Since the combination of fumes and water vapor arising from the asphalt presented a visible indicator of the movement of emissions, it was possible to qualitatively note the effectiveness of the wind as a source of natural ventilation. The "worst case" condition appeared to exist when the wind was blowing very lightly in the direction of paving. In this instance, the light wind, in combination with thermal currents from the hot asphalt, caused the emissions to slowly rise and be directed into the breathing zone of the paver operator. This observation was supported by the environmental data indicating instantaneous concentrations of hydrogen sulfide as high as 10 ppm, and 15 minute TWA concentrations of H<sub>2</sub>S as high as 6 ppm during this period of time. As would be expected, the optimum condition appeared to exist when the wind blew relatively strongly in a direction perpendicular to the paving operation, thereby creating a dilution of emissions while also directing them away from the workers.

#### 5. Comparison of Environmental Results With Results of Previous SEA Paving Emissions Studies

The results of the charcoal tube and membrane filter samples collected during the initial survey did not reveal the presence of any volatile sulfur containing organic compounds. Previous field studies conducted by the Bureau of Mines and Gulf Science and Technology Company, along with laboratory studies conducted by the Texas Transportation Institute have shown the same results.<sup>17, 2</sup>

Very little data reflecting the make-up or concentrations of particulate emissions during other SEA paving operations were noted in the literature. In one study, total particulate concentrations of 2.1 mg/M<sup>3</sup> for a paver operator, and 2.8 mg/M<sup>3</sup> for a screed operator were measured.<sup>18</sup> These values are somewhat lower than those found in this survey, but would not be considered unusual due to the many variables involved in SEA paving. In a second study, the percentage of total sulfate to total particulate in three samples was determined to be 1.5%, which is somewhat higher than the 0.3% found in this survey.<sup>19</sup>

Hydrogen sulfide and sulfur dioxide have been the two major contaminants that have been continually examined in almost all of the environmental studies reviewed. The majority of the studies appear to verify the relatively low concentrations of SO<sub>2</sub> found in this evaluation. With few exceptions, levels of SO<sub>2</sub> have not been detected or detected only in trace or very minute concentrations. One study did report SO<sub>2</sub> in personal breathing zone samples at TWA concentrations of 2.07 ppm for the paver operator, and 1.91 ppm for the screed operator.<sup>18</sup> In another study, detector tube measurements revealed SO<sub>2</sub> concentrations ranging from 0.5 to 20 ppm alongside the paver, but the high concentrations were attributed to a deliberate overheating of the paver screed, with very low concentrations detected under normal operating temperatures.<sup>2</sup>

Information related to hydrogen sulfide concentrations found in other SEA emissions studies is summarized in the following table.

<u>Concentration Range</u>	<u>Reference</u>
< LOD	18
< LOD - 0.9 ppm	20
< LOD - 2 ppm	21
< LOD - trace	22
< LOD - 2 ppm	19
< LOD - trace	23
< LOD - 8 ppm§	24
< LOD - 20 ppm†	17
Trace - 80 ppm*	2

< LOD: Less than Limit of Detection

§ - High value detected in process sample above screed

† - Momentary value in paver hopper (a non-personnel area) and above the screed during heating.

\* - High values were a result of overheating of the screed causing mix temperatures to exceed 320° F. When temperature was reduced to normal, concentrations detected were minimal.

The data from these studies indicates that concentrations of H<sub>2</sub>S should remain within the recommended environmental limits under normal circumstances. However, there is a potential for relatively high concentrations of H<sub>2</sub>S in some non-personnel areas such as the paver hopper, and in instances when proper temperature control of the SEA mixture is not maintained. One study did report relatively high exposures in the breathing zone of the paver operator during a period of time when no breeze was blowing and thermal currents were causing the emissions to rise upward.<sup>24</sup> This finding, as well as the overall findings of these studies, appear to be in agreement with the data collected in this evaluation.

#### B. Medical

Employees at the two sites included in the follow-up surveys were questioned as to their work experience with SEA paving and the presence of any health problems they felt were related to the paving. Since both of the paving operations were monitored in their early stages (average work experience 2 -4 days) and only one employee had previously worked on a SEA paving project, no health effects for longer-term exposure could be noted. However, essentially all of the employees reported eye irritation, and to a lesser degree, mucous membrane irritation, which was attributed to the SEA emissions. Many different factors were identified as influencing the degree of irritation experienced. These included ambient temperature, wind velocity and direction, and distance from paver. Some employees noted a gradual acclimation to the emissions, and reported less irritation as time went on. Additionally, of two employees questioned during the initial survey, one employee reported an upset stomach, while another reported a markedly increased appetite, with both symptoms being attributed to the sulfur. One employee who had worked with SEA paving the previous year noted a

feeling of the presence of dust in the lungs after SEA paving operations were ended. No instances of nosebleed, extreme nausea or vomiting were noted by the employees interviewed during these surveys.

Although a variety of types of respirators and eye protection were available at the paving sites which would have most likely reduced or alleviated the reported symptomatology, many employees did not utilize the equipment due to the warm ambient temperatures which they indicated made wearing of the personal protective equipment uncomfortable.

## VII. CONCLUSIONS

The results of the environmental survey indicated that concentrations of the various contaminants measured in the SEA emissions were generally below the corresponding environmental criteria. This finding is in agreement with the results reported in similar studies. However, despite the lack of exposures above existing environmental criteria, a significant amount of eye and upper respiratory mucous membrane irritation was still being experienced by the employees working at the paving operations. Based on the environmental survey results, it would appear that this symptomatology is most probably caused by airborne particulate sulfur which was determined to be the major component of the paving emissions (although in some instances, particularly when there was a lack of natural ventilation at the paver, concentrations of hydrogen sulfide approached levels that might further contribute to the irritative effects being experienced). Therefore, since levels of particulates below the nuisance dust criteria still resulted in a substantial amount of irritation, this criteria does not appear appropriate for SEA particulate emissions.

The environmental results indicated that the potential for the highest personal exposures was greatest for those employees working in the vicinity of the paver, with concentrations decreasing markedly with increasing distance from the paver. Although wind direction can have a substantial effect on exposures for the various jobs, on the average, the paver operator appears to be subjected to the highest levels of the emissions. Since this employee is required to remain in a fixed position on the paver, he is subjected to emissions from the truck unloading in front of the paver, as well as from the paver itself. The screed operator and laborers are also required to work in close proximity to the paver; however, these employees are allowed some degree of freedom of movement and are often able to avoid the emissions. The hot roller operator, although not subjected to the high concentrations experienced by the personnel in the vicinity of the paver, none the less, is often subjected to contaminant levels sufficient to cause some degree of irritation.

Although engineering controls are the preferred method for controlling occupational hazards, the very nature of paving operations do not lend themselves well to this type of control. Probably the most practical means of reducing exposures and alleviating irritation from the emissions would be through the use of personal protective equipment. Eye irritation can be controlled through the use of proper fitting eye protection. Respiratory irritation from the particulate sulfur can be prevented through the use of a properly fitted NIOSH/MSHA approved dust, fume, and mist respirator. (It is important that the respirator provide

protection against fumes since this appears to be the predominant form in which the sulfur is emitted.) Due to the circumstances under which such equipment must be worn (high heat etc.), employee comfort should be a major consideration in equipment selection and use.

Probably the single most important factor in maintaining safe levels of contaminants during SEA paving operations is the control of the SEA mix temperature. Several studies have shown that the levels of contaminants, particularly H<sub>2</sub>S and SO<sub>2</sub>, can increase greatly if asphalt mix temperatures rise above 300°F.<sup>2</sup> Providing that the asphalt transported to the paving site is below this temperature, the only other likely possibility for reaching this temperature would be through excessive use of the paver screed heater. Although the heater is normally utilized only during start-up or stop and go paving, if sufficient residual SEA material is present in the screed or paving hopper, it is possible for gaseous emissions to reach hazardous levels. Therefore, it is important that screed temperature be closely monitored to prevent overheating of the mix. If levels of hydrogen sulfide should be detected above the recommended evaluation criteria, and are unable to be controlled through other means, the use of supplied air respirators with a full face piece should be used, particularly for the paving operator.

The initial request indicated instances of nosebleeds, chapped and split lips, severe sunburn, and extreme nausea and vomiting among employees working with SEA, but these complaints were not noted during the course of this evaluation. Although much of this symptomatology can be associated with exposure to one or more of the contaminants evaluated in the survey, based on the concentrations of the substances measured during this evaluation, these effects would not be expected. However, it is possible that the conditions encountered in other surveys (e.g., asphalt temperature) were not adequately controlled and levels of emissions could have been sufficient to bring about these problems. Also, the lack of SEA paving experience among the groups of employees questioned in this evaluation may have precluded the ability to detect some problems which may have been related to a longer-term exposure. In the future, any health complaints experienced by employees working with SEA should be reported to supervisory personnel so that appropriate documentation can be made and follow-up actions can be taken to locate the source and a possible remedy for the problem.

It should be noted that this evaluation included only the paving or "lay down" aspects of SEA road construction. There are also additional hazards associated with the preparation of the asphalt at the "hot mix" plant and in the quality control laboratory. Many of the hazards associated with hot mix plants are the recognized hazards related to the storage and handling of liquid sulfur, as well as those hazards associated with asphalt preparation. There are a number of informational sources available which address the materials, construction, proper work practices, personal protective equipment, and emergency procedures recommended for SEA mixing plants.<sup>25,26,27,28,29</sup> One publication in particular "Field Environmental Evaluation Plan for Sulfur Use in Pavements", prepared for the Federal Highway Administration by the Texas Transportation Institute, provides detailed

information useful in evaluating risks and providing recommendations for mixing plants, quality control laboratories, and other areas where potential hazards from SEA may exist.<sup>30</sup> It is important that management and employees become familiar with the potential hazards and proper precautions associated with each aspect of these operations.

It is recognized that the SEA projects evaluated in this survey were of a "trial" nature, and that significant amounts of this type of paving in the State of Wisconsin is not anticipated until such time as it becomes more economically feasible. However, should SEA paving become more highly utilized in the future, appropriate steps should be taken to ensure employee safety and health.

### VIII. RECOMMENDATIONS

In order to alleviate the potential hazards associated with SEA paving operations, the following recommendations are made:

1. In all circumstances, SEA mix temperatures should be maintained below 300°F to ensure that gaseous emissions are minimized.
2. When utilized, the paver screed heater should be closely monitored to ensure that overheating of the asphalt does not occur.
3. Environmental monitoring should be conducted to ensure that concentrations of hydrogen sulfide and sulfur dioxide are maintained within the recommended levels. This monitoring should be conducted initially, periodically, and during situations which may warrant special testing; i.e., screed heating, lack of air movement, or employee complaints of symptomatology which might indicate high levels of these gases. The use of a continuous type of monitor with an audible alarm would provide an effective means of constantly monitoring these gasses; particularly, hydrogen sulfide.
4. Eye protection should be made available to any employees experiencing eye irritation from the SEA emissions. This should consist of dust tight safety goggles equipped with plastic or rubber frames.
5. Dust, fume, and mist respirators should be made available to any employees experiencing any upper respiratory tract irritation from the particulate emissions, especially during periods of diminished wind activity.
6. Employees should be informed of the hazards and safe work practices associated with SEA paving operations.

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1. Wisconsin Operating Engineers
2. Wisconsin Department of Transportation
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For the purposes of informing the affected employees, copies of the report should be posted in a prominent place accessible to the employees, for a period of 30 calendar days.

TABLE 1  
Results of Environmental Samples for Total Particulate and Total Sulfur  
 Collected During SEA Paving Operations

Sample Date (1982)	Sample Type	Sample Location or Job Title	Sample Duration (minutes)	Sample Volume (Liters)	TWA Concentration Total Particulate (mg/M3)	Sulfur Content (percent)
9/02	Area	Paver	188	282	5.4	100
9/02	Personal	Screed Operator	156	234	4.5	55
9/02	Area	Hot Roller	192	288	1.5	61
9/14	Process	Screed	40	60	59	NA
9/14	Area	Paver	294	441	2.9	100
9/14	Personal	Laborer	246	369	2.4	100
9/14	Area	Hot Roller	280	420	1.2	100
9/15	Area	Paver	343	515	5.6	100
9/15	Personal	Laborer	319	479	3.6	NA
9/15	Area	Hot Roller	363	545	0.5	100

Limit of Detection (LOD) = 0.01 milligrams (mg) per sample  
 NA = No analysis conducted

TABLE 2  
Results of Environmental Samples for Respirable Particulate and Respirable Sulfur  
 Collected During SEA Paving Operations

Sample Date (1982)	Sample Type	Sample Location or Job Title	Sample Duration (minutes)	Sample Volume (Liters)	TWA Concentration Resp. Particulate (mg/M3)	Sulfur Content (percent)
9/02	Area	Paver	188	320	5.1	100
9/02	Area	Hot Roller	192	326	0.2	100
9/14	Process	Screed	40	60	85	NA
9/14	Area	Paver	294	500	3.4	100
9/14	Area	Hot Roller	280	476	1.2	100
9/15	Area	Paver	343	583	4.0	100
9/15	Area	Hot Roller	363	617	0.4	100

LOD = 0.01 mg/sample

TABLE 3  
Results of Environmental Samples for Particulate Sulfates and Sulfites\*  
Collected During SEA Paving Operations

Sample Date (1982)	Sample Type	Sample Location	Sample Duration (minutes)	Sample Volume (Liters)	TWA Concentration Sulfates (mg/M3)
9/02	Process	Screed	91	137	0.12
9/02	Area	Paver	188	282	0.02
9/14	Area	Paver	294	441	0.01
9/15	Area	Paver	343	515	0.01

\*All samples for particulate sulfites were below the LOD of 4 ug/sample.

TABLE 4  
Results of Environmental Samples for Sulfur Dioxide  
Collected During SEA Paving Operations

Sample Date (1982)	Sample Type	Sample Location or Job Title	Sample Duration (minutes)	Sample Volume (Liters)	TWA Concentration Sulfur Dioxide (mg/M3)
9/02	Process	Screed	91	137	0.07
9/02	Area	Paver	188	282	0.04
9/02	Personal	Laborer	156	234	0.04
9/02	Area	Hot Roller	192	288	0.02
9/14	Area	Paver	294	441	0.02
9/14	Personal	Screed Operator	250	375	0.02
9/14	Area	Hot Roller	280	420	0.01
9/15	Area	Paver	343	515	0.03
9/15	Area	Hot Roller	363	545	0.01

LOD = 3 ug/sample

Table 5  
Results of Environmental Samples for Hydrogen Sulfide  
Collected During SEA Paving Operations  
(Consecutive 15 Minute Samples)

Sample Date (1982)	Sample Location	Number of Sampling Periods	Number of Periods H <sub>2</sub> S Detected	Highest H <sub>2</sub> S Concentration Detected (ppm)	Cumulative TWA Concentration (ppm)
9/02	Paver	9	2	2	0.3
9/02	Roller	10	<LOD	0	<LOD
9/14	Paver	NA	NA	NA	NA
9/14	Roller	<LOD	<LOD	<LOD	<LOD
9/15	Paver	21	14	6	1.9
9/15	Roller	23	<LOD	<LOD	<LOD

NA : No analysis conducted.

<LOD : Less than the LOD of 1 ppm for a 15 minute sampling period.

TABLE 6  
A Comparison of the Results of Side-By-Side Environmental Samples  
 Collected During SEA Paving Operations

Sample Date (1982)	Sample Type	Sample Location or Job Title	TWA Concentration Sulfates (mg/M3)	TWA Concentration Sulfur Dioxide (ppm)	TWA Concentration Hydrogen Sulfide (ppm)	TWA Concentration Total Particulate (mg/M3)/ % sulfur	TWA Concentration Resp. Particulate (mg/M3)/ % sulfur
9/02	Area	Paver	0.02	0.04	0.3	5.4 / 100	5.1 / 100
9/02	Area	Hot Roller	NA	0.02	<LOD	1.5 / 61	0.2 / 100
9/14	Area	Paver	0.01	0.02	NA	2.9 / 100	3.4 / 100
9/14	Area	Hot Roller	NA	0.01	<LOD	1.2 / 100	1.2 / 100
9/15	Area	Paver	0.01	0.03	1.9	5.6 / 100	4.0 / 100
9/15	Area	Hot Roller	NA	0.01	ND	0.5 / 100	0.4 / 100

\* Sample error involved - Respirable dust levels will not exceed the level of total dust in identical samples.

NA : No analysis conducted.

<LOD : Less than the LOD of 1 ppm for a 15 minute sampling period.

Table 7  
Summary of Environmental and Operational Parameters Monitored  
 During SEA Paving Operations

Survey Date (1982)	Wind Speed (mph)	Wind Description	Wind Direction (from/to)	Direction of Paving	Dry Bulb Temperature (°F)	Wet Bulb Temperature (°F)	Relative Humidity (%)	Asphalt* Temperature (°F)
9/02	5 - 10	gusting	northwest	East - West	73	60	46	240
9/14	3 - 5	steady	northeast	East - West	60	57	83	260
9/15	< 3	steady	variable	East - West	58	54	77	270

\*Temperature measurement taken in unrolled asphalt roadbed directly behind paver.