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# Summary of Health Practices: The Use of Petroleum Asphalt in the Hot-Mix Paving Industry

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# Abstract

This document presents a review of the literature regarding aspects of the health of man and the environment as related to the use of asphalt cements in the paving industry. The information in this state-of-the-art report includes the following: (a) studies on the exposure of man and the environment to paving asphalt emissions; and (b) potentially associated effects on human health identified through clinical and epidemiological reports and animal toxicological studies. This report also includes discussions on the presence and type of polynuclear aromatic hydrocarbons (PAHs) in paving asphalts and asphalt emissions. Finally, several areas of needed research were suggested. This report was prepared by The University of Texas at Austin Asphalt Research Program of the Center For Transportation Research under contract with the Strategic Highway Research Program.

# Chapter 1 Introduction

## The Strategic Highway Research Program

Concern for the continuing deterioration of the nation's highway and bridge infrastructure resulted in the establishment of the Strategic Highway Research Program (SHRP). SHRP is a highly focused, specially funded program that concentrates on four critical areas of highway research concerning pavements and bridges (Table 1.1): asphalt characteristics, pavement performance, concrete and structures, and highway operations and maintenance. The primary function of SHRP is to concentrate highly innovative research approaches to achieve significant gains in these few specific areas of highway technology rather than accomplish incremental research advances in many areas.

## Asphalt Research Program

In-depth research of asphaltic materials covers such a broad range of considerations that a contract to manage, coordinate, and monitor the Asphalt Research Program and to assure proper interaction with SHRP was necessary. This need was resolved by the formation of Contract A-001; "Improved Asphaltic Materials: Experiment Design, Coordination, and Control of Experimental Materials". This contract was awarded to The University of Texas at Austin's (UT) Center for Transportation Research as a five-year project to commence operation on October 27, 1987 (UT, 1987) with Dr. Thomas W. Kennedy as the principal investigator.

The objectives of the A-001 contract are to coordinate the varied complex asphalt-research activities of SHRP, to interact closely with all of the asphalt research contracts to guide the research toward improvements that are technologically and economically feasible, to develop performance-based asphalt binder and mixture specifications, and to plan and enact a strategy to ensure rapid field use of key results. Additional specific tasks were included, one of which, Task C1, was to develop a summary of the information on the Health and Safety factors to consider in using asphalt binders.

## Summary of Health and Safety Practices

The overall objective of Task C1 was to develop as complete a summary as possible of the current knowledge regarding aspects of the health and safety of man and the environment associated with the use of asphalt binders in pavement construction. The specific objectives of this task were to: (a) summarize and evaluate the existing base of knowledge, (b) determine, to the extent possible, the significance of asphalt paving practices on the health and safety of man and the environment, (c) identify areas of primary concern, and (d) suggest areas of needed research. No new research was planned for this task. Rather, a state-of-the-art report was to be developed based on a review of the literature.

This task involved a broad base health related survey performed under the supervision, direction and guidance of Dr. Raymond C. Loehr and a safety survey performed by Mr. James A. Scherocman. Dr. Loehr, a member of the National Academy of Engineering, is a senior faculty member of the Environmental and Water Resources Engineering Program in the Department of Civil Engineering at the University of Texas at Austin. Working with Dr. Loehr was Mr. R. Marcus Barksdale, a graduate student responsible for performing the health survey and preparing the draft reports. Mr. Scherocman is a nationally recognized consultant with many years of experience in the asphalt construction industry.

## Scope

The scope of this study covers several topics: (a) the methods by which petroleum-derived asphalt binders are used in road construction with hot-mix asphalt pavements. Such construction methods are defined in this report to include the handling and transportation of paving-grade asphalt cements, the production of hot-mix asphalt concrete, and the placement of hot-mix asphalt concrete to form pavement surfaces; (b) issues on the safety of workers involved with asphalt hot-mix pavement construction, (c) exposures of workers, the general public, and the environment to emissions from construction processes and from the wear and degradation of hot-mix asphalt pavements and waste materials; and (d) potentially adverse effects on human health and the environment associated with exposure to the various asphalt emissions.

This report focuses on the use of paving-grade asphalt cements in hot-mix asphalt concrete. The use of modified asphalt cements, such as emulsions and cutbacks, and the employment of other activities in the paving industry, such as asphalt refining and testing procedures, are acknowledged in this report and pertinent sources are cited for further reference, but these topics are not discussed.

Not included in this report is the exposure of man or the environment to materials other than asphalt as used in the paving industry (e.g., aggregate dusts). Also not pertinent to the scope are the uses of asphalt in applications other than paving operations (e.g., roofing, paints, or pipe coatings).

## Literature Search

The information reported in this study was based on references identified from as complete as possible health-related surveys of the published literature. These surveys included: (a) literature searches performed by the UT Center for Transportation Research, the National Safety Council, Shell Oil Company, and The Asphalt Institute utilizing the data bases (Table 1.2), (b) sources that were referenced by other articles, and (c) sources recommended by colleagues. Most of the references used in this report were obtained from the library system at The University of Texas at Austin and through Inter-Library Services. However, several potentially useful references could not be obtained (Appendix A). Some of these sources are discussed in this report as they were cited in other available sources. They are noted in the bibliography. An additional list of potentially useful articles written in foreign languages also was compiled (Appendix B). English translations of these references were not available for incorporation into this report and their usefulness is dependent upon their definition of bitumen or asphalt.

# Chapter 2 Background

This chapter is to provide background information on the topics presented in this report. Included are discussions on the characteristics and composition of asphalts within the scope of this study, its production and use in road construction, and potential adverse health risks posed by compounds contained in asphalt and within the boundaries of use described.

## Description of Asphalt

Asphalt are viscous liquids or solids consisting primarily of hydrocarbons and their derivatives, which are soluble in carbon disulfide. They are substantially non-volatile at ambient temperatures and soften gradually when heated. Asphalts are dark brown to black in color and possess waterproofing and adhesive properties. Asphalts are obtained by refinery processes from petroleum and also are found as natural deposits, often associated with mineral matter.

In North America and in this report, the term "asphalt" is associated with the material previously described. The terms "bitumen" and "asphaltic bitumen" are synonymous words used outside North America to identify both petroleum and coal based products. This often causes confusion outside North America the term asphalt is used.

Asphalts in this report should not be confused with coal-derived products such as coal-tar and coal-tar pitch. These substances are by-products of the high-temperature destructive distillation, also called carbonization or coking, of bituminous coals. They are similar to asphalts in appearance and adhesive characteristics, but are substantially different in chemical composition. In Europe, coal-derived residues are sometimes blended with petroleum asphalts for use in both road construction and industrial applications. This practice has virtually ceased in North America. Coal-tar and derived products have been described in detail by the International Agency for Research on Cancer (IARC) (1985). A concise review of the differences between asphalts and coal-tar products also has been given by Puzinauskas and Corbett (1978).

Similarly, asphalt should not be confused with petroleum pitches, which are often highly aromatic residues produced by the thermal cracking, coking, or oxidation of selected petroleum fractions. Petroleum pitches are principally used as binders in the manufacture of metallurgical electrodes. The term "petroleum pitch" is used to describe different materials in different areas of application.

## Chemical Composition of Asphalt

The chemical composition of asphalt depends both on the composition of the original crude oil and on the processes used during refining. Asphalts can generally be described as complex mixtures containing predominantly cyclic hydrocarbons and a lesser quantity of saturated components. Also found in asphalts are heteromolecules that contain sulfur, nitrogen, oxygen, and trace amounts of vanadium, nickel and iron. Typical contents of chemical elements found in asphalts are given in Table 2.1.

## Broad Chemical Composition

The chemical characterization of asphalts are based on their separation into generic classes of compounds that are complex mixtures; not well-defined chemical species. Numerous separation techniques are reported in the literature. However, data from different methods are not interchangeable since the broad compound classes are empirically defined by many factors involved in the partitioning processes. These factors may include: (a) the characters of the solvents, eluents, and absorbents, (b) ratios of solvent to asphalt and eluent to adsorbent, (c) the use and type of filters, and (d) temperature.

The American Society for Testing and Materials (ASTM) (1986) has developed a separation technique that is widely used in North America. Test Method D 4124, Standard Test Methods For Separation Of Asphalt Into Four Fractions, allows asphalt to be partitioned into asphaltene, polar aromatic, naphthene aromatic, and saturate fraction. Typical levels of these fractions are given in Table 2.2.

Asphaltenes are brown to black amorphous solids containing sulfur, nitrogen, oxygen, and trace elements of metals, in addition to carbon and hydrogen atoms. They are highly polar materials with molecular weights of 2000 to 5000 grams per mole (g/mol) and consist of highly condensed aromatic ring structures.

Polar aromatics, also called resins, are dark-colored solids or semi-solids that act as dispersing agents or peptizers for the asphaltenes. They contain a wide distribution of aromatic and naphthenic molecular structures with polar groups. Their molecular weights range from 800 to 2000 g/mol.

Naphthene aromatics, also called cyclics, are dark viscous liquids with molecular structures that contain aromatic and naphthenic aromatic nuclei with side chain constituents. They exhibit molecular weights of 500 to 900 g/mol and represent the major portion of the dispersion medium for the asphaltenes.

Saturates are the straight- and branched-chain aliphatic hydrocarbons present in asphalts, together with alkyl naphthenes and some alkyl aromatics. The average molecular weight range is approximate to the cyclics, and the components include both waxy and non-waxy saturates.

Asphalts have been described as colloidal systems consisting of asphaltene micelles dispersed in a lower molecular weight oily medium (maltenes). The micelles possess an adsorbed sheath of aromatic resins of high molecular weight that act as a stabilizing solvating layer. Away from the center of the micelles there is a gradual transition to less aromatic resins, cyclics, and saturates.

## Polynuclear Aromatic Hydrocarbons

Polynuclear aromatic hydrocarbons (PAHs) are ubiquitous in nature and are constituents of fossil fuels such as petroleum and coal. They have been shown to generate adverse health effects in animals and man. This topic is discussed further in Section 2.5.

PAHs are composed of two or more fused (condensed) aromatic hydrocarbon rings. Aromatic rings are termed "cyclic" which can cause confusion with the generic class of hydrocarbon compounds known by the same word. Ideally, PAHs consist only of carbon and hydrogen, however, in many cases they contain one or more ring positions in which a carbon atom has been replaced by an atom of sulfur, nitrogen, or oxygen. The terms "heteromolecule" and "hetercyclic" often are used to describe these PAH derivatives.

Under the proper conditions, PAHs and their derivatives can be formed through the thermal degradation of organic materials. At high temperatures, relatively few heterocyclic compounds are formed, while at lower temperatures the number of substituents tends to increase (Figure 2.1).

Generally, PAHs are present in asphalts in more limited amounts than in crude oils (Bingham et al., 1979). This situation results from the various techniques employed in petroleum refining that (a) remove the majority of compounds of lower molecular weight and boiling-point, including PAHs, and (b) are conducted at low temperatures for short periods of time which limit PAH formation (IARC,1985). The levels of PAHs analyzed in several asphalts are shown in Tables 2.3 and 2.4. For comparison, PAH levels in two coal-tar pitches also are shown (Table 2.3). Note that asphalts contain PAHs in quantities of two to five orders of magnitude less than the amounts in coal-tar pitches.

## Asphalt Production

Today, most asphalts as defined in this report are derived from crude petroleum oils, using manufacturing processes that generally avoid thermal degradation. They are produced from crude oils that give substantial amounts of heavy residue, typically from 10-50% (IARC, 1985). The processes incorporated in asphalt production are summarized below and illustrated in Figure 2.2. A more detailed account of these processes has been given by Chipperfield (1984).

Atmospheric distillation is the first stage in petroleum refining. In this process, crude feedstock is heated under pressure and sprayed into a distillation tower where it experiences temperature and pressure gradients and flash distills. The more volatile components migrate to the cooled top of the tower and the less volatile to the heated base, where they are collected as residuum (Goodger, 1975). The atmospheric residue of very heavy crudes is sometimes used directly for asphalt production.

Generally, atmospheric residues are distilled further by employing a vacuum distillation tower. This process increases the pressure gradient without increasing distillation temperatures, thereby preventing thermal degradation of the distillates and residue. Sometimes steam is injected into the atmospheric residue to aid in distillation by adding its own partial pressure, thus lowering the partial pressures of the components and further increasing the pressure gradient (Goodger, 1975). Vacuum and steam-refined residues from some crude oils meet performance requirements for particular asphalt applications.

Some crudes contain components of high boiling-point which are difficult to recover even when high vacuum is used. Such materials are separated from vacuum residue using solvents such as propane or butane. Solvent-precipitated asphalts have a higher content of asphaltenes than the vacuum residues from which they are produced, but a lower content of saturates than would be obtained by distillation of the vacuum residue (King et al., 1984).

Air-blowing processes are used to provide special physical properties to asphalts. The blowing process dehydrogenates the distillation residue, resulting in oxidation and condensation polymerization reactions. The content of asphaltenes is considerably increased, while the content of cyclics is decreased (Corbett, 1975). King et al. (1984) cited these changes as evidence that the cyclics are converted to resins which in turn are converted to asphaltenes. Limited air-blowing is required in some cases to produce asphalts from the available crude with the qualities necessary for use in paving applications.

Asphalts are classified by the refining and processing methods used in their production. Controlled blending of selected asphalts and other substances also is performed to create different classes of asphalt. Within each class, asphalts are graded according to performance-based specification tests related to their intended applications. These tests measure physical properties such as penetration, ductility, viscosity, and softening-point. Most of these tests are standards adopted and described by the American Society For Testing and Materials (ASTM) and the American Association of State Highway and Transportation Officials (AASHTO). The most important classifications of asphalt are discussed in Appendix D.

The principal uses of asphalt are shown in Figure 2.3 with respect to the various grades available. Note that many asphalts used in road construction cover a wide range of grades while asphalts used specifically for asphalt concrete mixes are limited to a very narrow range. Regardless of the grades among class 1 and class 2 asphalts, the PAH contents are roughly the same (Tables 2.3 and 2.4).

## Asphalt Concrete Production and Paving Operations

Asphalt that is suitable for use in pavement construction is commonly called "asphalt cement" or "asphalt binder". Processed at the petroleum refinery, it is kept in storage tanks until needed. Transportation to the user can be by railroad tank cars or by highway using tanker trucks. Asphalt cement is transferred as a liquid between storage and transport tanks through pumping operations. To maintain pumping ability, it is kept heated to a suitable temperature, typically not exceeding 350°F (177°C) (The Asphalt Institute, 1989a).

Asphalt concrete is the most commonly used asphalt product in road construction. It consists of a mixture of well-graded, high-quality aggregate and a small amount of asphalt cement (Figure 2.4). In asphalt concrete mixes, both the aggregates and the asphalt are heated before combining them. This material, commonly called "hot-mix", is transported directly to the construction site after production. Another material, called "hot-mix,cold-mix", is produced by heating the aggregates to lesser temperatures and mixing them with asphalt cement that has been diluted with petroleum distillates (cutback asphalt) or emulsified with water (emulsified asphalt). These materials may be stored for some time before application and are primarily used as road maintenance materials. They develop strength as the solvent or water evaporates from the mixture (The Asphalt Institute, 1989a). Discussion of cutback and emulsified asphalts is beyond the scope of this report.

Hot-mix asphalt concrete, brought to the paving site in trucks, is deposited directly into a paving machine or in windrows in front of the paver. The paver (Figure 2.5) then evenly spreads the mix as it moves forward. Approximate lay-down temperatures for hot-mix asphalt concrete are near 135-148°C (275-300°F). During the laying of asphalt concrete, the screed plate, which provides a smooth surface and the correct designed depth of the asphalt concrete layer, must be heated to prevent the asphalt cement from sticking to it. This is commonly done by burning a petroleum distillate, such as butane or diesel fuel, thereby keeping the screed plate quite hot and the asphalt cement fluid. Once the mixture is spread, it is compacted to the required density before it cools. Compaction is accomplished by repetitive rolling with steel-wheeled and rubber-tire rollers. Some work must be performed by hand to place the mixture in areas not reached by the paver and to correct for random errors in placement. This may involve shoveling and raking the asphalt concrete and compacting the mix by hand tamping or with portable vibrating plates (The Asphalt Institute, 1989a).

All of the processes involved in the transportation, production, and application of asphalt cement and hot-mix asphalt concrete generate emissions to which workers and the environment are exposed. Measurements of the character and magnitude of these emissions are discussed in Chapter 3.

## PAH Metabolisis

Under certain conditions, after exposure to certain materials derived from fossil fuels, such as petroleum and coal, in some cases evidence of mutagenicity and carcinogenicity has been observed in humans and experimental animals. This mutagenic/carcinogenic potential appears to be attributable, at least in part, to PAHs (National Academy of Sciences, 1972; IARC, 1973). Chapter 5 contains discussions of the reported and observed health effects in both humans and laboratory animals following exposure to emissions from paving-grade asphalt.

The following discussion is a brief summation of the metabolisis of the PAH compounds that are present in small amounts in asphalts when proper conditions exist. A more detailed study would relate primarily to materials outside the scope of this report.

Bingham et al. (1976) reported that in petroleum the 4- to 5-ring PAHs are essential for the production of tumors (Table 2.5). Other compounds were noted as cocarcinogens, acting synergistically with carcinogens to increase tumor production, and as inhibitors, acting antagonistically with carcinogens to decrease tumor production. Through laboratory studies on experimental animals, the relative carcinogenicity of many individual PAH compounds has been determined (Table 2.6). It is important to note that only some PAHs exhibit a potential for carcinogenic activity and only when the proper conditions are present. These compounds tend to have high molecular weights and range from 4 to 6 rings. Also note that the alkylated PAHs (e.g.,methyl-compounds) typically exhibit greater activity than their parent compounds.

The carcinogenic potential of certain PAH compounds has been recognized for decades, however, details of the mechanisms of PAH metabolisis and carcinogenesis have only recently become better understood.

## Summary

Asphalt is a complex mixture of organic compounds, primarily composed of high boiling point and high molecular weight hydrocarbons, whose molecules are combinations of the familiar petroleum structural building units. Its physical behavior can be explained by considering it a colloidal system whose properties are influenced by the interactions of various empirically defined generic compound classes.

Asphalt's overall composition depends on the composition of the crude petroleum from which it is obtained, as well as the techniques used to refine and process it. Atmospheric, vacuum, and steam distillation removes the lower molecular weight hydrocarbons from the crude oil, leaving the heavier compounds as an asphaltic residue. Solvent precipitation removes some saturated compounds while leaving aromatic ring structures. Air-blowing transforms saturates into cyclics and cyclics into asphaltenes. Through the various refining and processing techniques, a class of compounds called PAHs generally are reduced in asphalts to lesser quantities than are present in the petroleum crude.

Asphalts are used to form products for many applications, including the use of hot-mix asphalt concrete in road construction and maintenance. The methods employed in transporting asphalt cement, producing hot-mix asphalt concrete, and applying the hot-mix as a pavement surface can generate emissions to which humans (Chapter 3) and the environment (Chapter 5) are exposed when proper conditions exist. Since asphalt contains PAHs, the potential exists that when these conditions do occur these emissions also may contain PAHs. The potential for adverse health effects in man and the environment from exposure to PAHs is discussed in Chapters 4 and 5, respectively.

# Chapter 3 Occupational Exposure Monitoring

This chapter discusses the direct exposure of man to emissions generated from the use of petroleum asphalt in the paving industry. Included in this chapter are discussions on: (a) existing national exposure standards in the world, (b) reported attempts to identify the physical character and magnitude of asphalt emissions, and (c) reported attempts to measure the extent of biological exposure to mutagenic / carcinogenic compounds in asphalt emissions.

## Exposure Standards

The possibility for hazards associated with occupational exposure to asphalt fumes has been recognized for some time. In responding to these possible health hazards, agencies charged with the protection of human health have established exposure standards in several countries. Table 3.1 lists the present standards for asphalt fumes in comparison with standards for other substances that are contained in asphalt fumes.

In America, the American Conference of Governmental Industrial Hygienists, Inc. (ACGIH) recommended threshold limit values (TLVs) for asphalt fumes of 5 $mg/m^3$ based on an 8-hour time-weighted-average (TWA) and 10 $mg/m^3$ based on short-term exposure. These TLVs refer to the airborne concentrations to which many, but not all, workers may be exposed, for 8-hour workdays, 40-hours per week for a lifetime, without adverse health effects (Craft, 1983). The National Institute for Occupational Safety and Health (NIOSH) also has recommended a maximum ceiling limit of 5 $mg/m^3$, based on a 15 minute average concentration. In 1988, the Occupational Safety and Health Administration (OSHA) announced its proposal to incorporate the recommended 8-hour TWA limit of 5 $mg/m^3$ into national legislation. This proposal is currently under review.

## Emissions Sampling

Direct exposure of man to asphalt emissions is defined in this review as the occupational exposure that workers may experience while performing the various duties required in the asphalt paving industry. In the occupational environment, workers may be exposed to asphalt emissions by inhalation, skin contact, and ingestion. As a person breathes, vapors and airborne particulate matter can be inhaled. These emissions, as well as the asphalt itself, may contact unprotected skin during normal work routines. Both inhalation and skin contact can lead to ingestion of substances through contact with food or entrapment in saliva and nasal mucous, which are subsequently swallowed. The contents of these emissions may include both mineral and organic matter. The material presented in this section contains a summary of the reports that concern direct occupational exposure to asphalt emissions, including the monitoring and characterization of such emissions from the various processes in the asphalt paving industry.

## Asphalt Production

Asphalt cements used in paving mixtures are produced by the refining processes discussed in Chapter 2. Several investigations have been conducted to characterize the emissions generated by these processes and to monitor the occupational exposure of refinery workers. Discussion of asphalt production, however, is beyond the scope of this report. Further information on this phase is available from Futagaki (1981), NIOSH (1980a), NIOSH (1980b), and Von Lehmden et al. (1965).

## Handling and Transporting Asphalt Cement

Asphalt cement is typically transported from petroleum refineries to hot-mix production facilities using vehicles such as road-tanker trucks or railroad tank cars. To transfer the asphalt between storage tanks and transport vehicles, the asphalt material is heated to suitable temperatures. The occupational exposures of primary concern to workers involved in this process are the inhalation of vapors from the transport vessel and skin contact with vapors or potential splashes and spills of hot material.

Brandt, et al. (1985) performed extensive sampling of asphalt emissions from various processes using asphalt binders. Inhalation of fumes and particulate matter was common to all jobs. There also was a varying degree of skin contact. The primary aim of the sampling strategy for all of the surveys was to collect personal samples of airborne particulate within 20 cm of the nose and mouth of workers while performing various jobs associated with hot-mix paving operations. Samples were taken for the maximum time allowed for the average accomplishment of the specific task. The sampling strategy provided data on average concentrations for the time given, adjusted to the average work shift where practicable (time-weighted over 8 hours), and assuming that no further exposure occurred during that 24 hour period. To ensure that valid data were produced, sampling was closely supervised by trained personnel, who also assisted with interpretation of the results.

One of the processes surveyed was truck-tanker loading. In an outdoor petroleum refinery loading station, air samples of the working environment were taken as hot asphalt cement was loaded into the tankers. The temperature of the asphalt varied from 170° C to 210° C (338° F to 410° F) depending on the grade of material, which was not reported. On the first day of the two day survey, one operator was engaged in loading while another operator was occupied with miscellaneous duties such as checking tank levels. On the second day the operators switched duties. One personal air sample was obtained for each worker on each day of the survey, totaling four samples.

The samples were analyzed for particle size distribution (Table 3.2). Most of the particles were less than 12.5 $\mu$m, with the majority between 3.8 $\mu$m and 1.2 $\mu$m. Sanders (1986) discussed that only particles $< 10$ $\mu$m in diameter are considered in the respirable range, with the exception of long fibers such as asbestos. Furthermore, particles in the range of 0.1 $\mu$m to 2.0 $\mu$m appear to have the greatest potential for deep lung penetration and retention (Fig. 3.1) and thus are of greatest interest in asphalt fume exposure studies. Talcott and Harger (1980) noted that the direct-acting mutagenicity of ambient particulate is associated predominantly with the respirable particle size range (defined as particles $< 2$ $\mu$m) on which PAHs preferentially accumulate through condensation processes (Van Cauwenberghe, 1985). However, the bioavailability of adsorbed PAHs also depends on the resorption efficiency of the lung tissue. Increased water solubilities of polar PAH derivatives (Chapter 5) will probably promote resorption after inhalation, but also will facilitate wash-out removal from the particulate (Van Cauwenberghe, 1985).

Analyses of total particulate matter (TPM) (Table 3.3) indicated that particulate exposure was roughly twice as great for loading operations than for other duties. Analyses of benzene soluble matter (BSM) also showed that a larger proportion of the TPM from loading operations was composed of organic materials, that include PAH compounds, compared to the TPM from other duties. Although the loading operator's exposure to organic matter was approximately seven times the other worker's exposure, the values were well below any published standard (Table 3.1)

Analyses of the sampled organic matter for 14 PAH compounds (Table 3.4) detected phenanthrene and benzo[g,h,i]perylene in the greatest quantities. These compounds are thought to be biologically inactive (Table 2.6). Detected in the next greatest amounts were chrysene and benzo[a]pyrene, carcinogenic PAHs known to be slightly active and very active, respectively. It is recognized that these values were based on a very limited sampling.

## Hot-Mix Asphalt Concrete Production

Hot-mix asphalt concrete consists of well-graded mineral aggregates thoroughly blended with a small amount of a paving-grade asphalt cement. It is typically produced through automated processes at central mixing facilities. Emissions from hot-mix production are directed through pollution-control devices that may include water-spray towers, centrifugal scrubbers, bag filters, and electrostatic precipitators. Treated emissions are then released to the atmosphere, where they are subject to the prevailing meteorological conditions.

Investigation of the literature has revealed no sources regarding the effect of direct exposures on workers at the hot-mix production facility, neither to treated emissions, fugitive emissions, nor during maintenance and repair activities. Generally, workers may receive exposure only to treated and fugitive emissions by inhalation. It is possible but unlikely that they may be exposed by inhalation and skin contact during maintenance and repair of equipment.

Treated emissions have been partially characterized in five identifiable reports, but these detailed discussions of the available pollution control devices are not pertinent to the scope of this report. The interested reader is referred to Von Lehmden et al. (1965), Crim and Snowden (1971), Kinsey (1976), Khan and Hughes (1977), and Beggs (1981) for further information on the topic.

Finally, two reports have been identified regarding the character of fugitive emissions from asphalt hot-mix plants. Doss et al. (1980) provided a descriptive account of fugitive atmospheric emissions when using emulsified asphalts to produce asphalt concrete mixes which are primarily produced for long term stockpiling for maintenance use. Discussion on the use of emulsified asphalts, however, is also beyond the scope of this report.

Puzinauskas and Corbett (1975) also reported fugitive emissions sampling at asphalt hot-mix batch plants. At one plant in Edison, New Jersey, six complete sets of samplings were obtained, two on each of three separate days, within a three-month period. The sampling location was the space between the pugmill mixer and the skip-hoist bucket. The latter was used to transport freshly mixed asphaltic concrete to hot storage bins. During the first sampling day, the space was not enclosed as is normal in asphalt plant operations. On the other sampling days the space was enclosed by hanging a polyethylene shroud on all four sides.

To provide sampling of asphalt paving materials formed from asphalt cements differing in physical characteristics from those used at the Edison plant, the study was extended to include sampling at another batch plant in Greensboro, North Carolina. At this plant, two complete samplings were obtained on one day in the space between an enclosed screw-type conveyer that transported fresh asphalt concrete from the pugmill and a bucket elevator that carried the asphalt mix to hot storage bins. This sampling space also was enclosed with a polyethylene shroud.

The results of sample analyses given in Table 3.5 represent either ranges or maximum values found for the indicated substances. Generally, all substances listed were found at very low concentrations even though the samplings were performed under exaggerated conditions. The authors noted that the values for methane and carbon monoxide were comparable to concentrations present in ambient air. They also noted that the greater benzene soluble fraction of particulate from the Greensboro plant could be associated with the higher volatility of the asphalt used in that plant. The low or absent concentrations of metals in the emissions suggest that they remain in the non-volatile, high-molecular weight components of asphalt (asphaltenes) during mixing operations.

Tests showed that PAH compounds were found in very small quantities at both sites. The distribution of PAH compounds present (Table 3.6) shows that the most abundant compound in the emissions was pyrene. Other compounds such as benz[a]anthracene, benzo[a]pyrene, and benzo[e]pyrene were present in the emissions in very small amounts.

## Handling and Transporting Hot-Mix Asphalt Concrete

Handling and transporting asphalt paving mixtures from the hot-mix plant to the job-site usually is accomplished by trucks. Exposure to the environment from this transportation such as spills of material caused by accidents and releases of volatile constituents to the atmosphere from uncovered truck beds are likely to be at a very low level and insignificant.Investigation of the literature has uncovered only one source that approximates human exposure to asphalt emissions from handling and transporting hot-mix asphalt concrete.

The National Asphalt Pavement Association (NAPA) (1989) reported the sampling of asphalt fumes at a hot-mix plant where the asphalt concrete mixture was loaded into transport vehicles. Two facilities were chosen for study: a batch-mix plant in Florida and a drum-mix plant in Maryland. At the Florida facility three personal samplers were placed in fixed positions around the transport vehicles so as to not directly measure contributions from vehicle exhausts. At the Maryland facility, three personal samplers were placed around the loading area in unspecified locations.

The personal samplers incorporated two types of filters arranged in series. Ambient air was drawn through the first filter to remove particulate matter, and then through the second filter to trap gaseous hydrocarbons. The first filter was analyzed for TPM and BSM while the second was analyzed for the content of 17 PAH compounds. The quantities of PAHs constituting the BSM fraction of the particulate was not determined.

The results from the Florida sampling (Table 3.7) indicate that significant quantities of particulate matter were detected while the mass of benzene soluble organic matter was below the detection limit for the method of analysis. In contrast, the Maryland sampling results (Table 3.8) indicated much lower TPM in the ambient air while the sampled TPM contained significant amounts of organic matter. Gaseous PAHs were not detected in either study.

Three factors which may explain the differences in TPM and BSM between the two facilities: (1) The Maryland plant used a less viscous grade of asphalt cement that would have allowed greater volatilization of hydrocarbons from the hot-mix, (2) The Maryland plant also processed the hot-mix at higher temperatures than the Florida plant, resulting in higher hydrocarbon emissions; and (3) The winds also were considerably stronger during the Florida sampling, which could have resulted in a much higher concentration of airborne particulate matter available for collection during sampling.

There was an absence of detectable amounts of PAHs in the samples of collected gaseous hydrocarbons analyzed for PAH content. The organic fractions of the sampled particulate were not measured for PAH content.

## Hot-Mix Asphalt Concrete Paving Operations

Placement of hot-mix asphalt concrete is a worker-intensive operation. The material, brought to the paving site in trucks, is deposited into a paving machine or in windrows in front of the paver. The material is then evenly spread with a smooth and uniform surface as the paver moves forward. Often, the placement of material, particularly in small areas, must be adjusted using shovels and rakes. When placement is complete, the material is compacted and allowed to cool. The workers encountering the greatest degree of exposure typically consist of the paver operator, roller operators, screedmen, and rakers.

Puzinauskas (1980) attempted to characterize occupational exposures to asphalt fumes during typical paving operations. The paving projects consisted of overlaying existing urban pavements with surface courses and the construction of base courses. Portable personal samplers were used to obtain air samples in the breathing zone of the workers. Sampling periods ranged from about one hour to three and one-half hours, averaging about two hours per sampling period for each worker.

The paver operator, the raker, and the screedman were selected for monitoring. During the paving process, the paver operator was seated on top of the paving machine in a stationary position between the paver hopper (receiving the hot mixture from the transport truck) and the paver screed (discharging partially consolidated hot-mix). The exposure of the paver operator was monitored during 14 sampling days. The raker's duties involved manual correction of the spread mixture with hand tools such as rakes and lutes. Normally, the raker was located in close proximity to the paving machine screed and the freshly-spread mixture. However, occasionally this worker also performed other duties away from the paver. The raker's exposure was monitored during the first seven sampling days. The screedman operated the paver screed, and normally was located directly above the auger and the freshly-spread mixture. During operation of the paver, the screedman would adjust screw-jacks to control the thickness of the spread mixture. This worker also worked to control the width of the spread mixture. The screedman's exposure to emissions was measured during the last seven field sampling days.

The samples were analyzed for airborne particulate concentration. From the results (Table 3.9) it is apparent that the paver operator received the greatest exposure to paving emissions since, during the 14 tests, his exposure averaged 1.26 $mg/m^3$ and ranged from 0.15 $mg/m^3$ to 5.61 $mg/m^3$. Puzinauskas noted that this maximum value appeared to be abnormal compared to the other data and might have been caused by the deposit of a dust particle on the filter. The raker on average, was exposed to particulate of 0.93 $mg/m^3$, (ranging from 0.25 $mg/m^3$ to 3.46 $mg/m^3$) and the screedman was exposed to an average of 0.83 $mg/m^3$ (ranging from 0.33 $mg/m^3$ to 1.47 $mg/m^3$). From the data, the raker's maximum value appears to be an outlier similar to the outlier for the paver operator. Substantial amounts of dust were noted in eight of the 14 tests, but no substantial differences were seen in the particulate concentrations.

Puzinauskas noted that other sources of emissions may have contributed to the total particulate that were measured, but the significance of these sources and their contribution to the actual emissions from asphalt could not be evaluated. These sources include tobacco smoking by some of the monitored workers and exhaust fumes from both construction equipment and passing traffic.

Attempts also were made to extract and measure the benzene-soluble portion of the sampled particulate. However, all of the samples were stored for 8 to 10 weeks before they were analyzed. This lapse allowed the original mass of the exposed filters to change substantially through evaporation or other causes, thereby invalidating the analyses.

Malaiyandi et al. (1982) monitored asphalt fumes during asphalt paving operations. The study involved collecting samples of air in the breathing zones of two workers during paving operations and of the ambient air. Further details of the samplings were not reported. The results (Table 3.10) indicated that the workers were exposed to higher levels of most of the measured PAHs than those found in ambient air. The total PAH concentrations also were several times the amount in ambient air. At both sites, the paver operator received significantly higher exposure to PAHs than did the level wheel operator. It could not be determined from the report what time periods were used for the sampling.

Brandt et al. (1985) sampled bitumen fumes from various construction processes that used asphalt binders. Besides tanker-truck loading, (Section 3.1.3) two other processes were investigated that involved road maintenance and construction. These surveys included surface dressing and asphalt paving operations. The sampling strategy and analysis techniques were performed as discussed for tanker-truck loading.

Surface dressing operations involved the use of cutback asphalts which are not in the scope of this report. Asphalt paving operations involved pavement construction using three different material mixtures. (1) Hot asphalt in a granite/asphalt mixture was delivered at 135° C (275° F) as a wearing course to the road surface. The material passed from the front hopper of a paver by a screw feed over a heated scraper bar. The paver driver sat on top of the vehicle and stood on the rear scraper bar or above the screw during preheating. Kerosene was used to prevent asphalt from sticking to the machine feed hopper. A chipper vehicle followed closely behind. (2) A similar procedure was followed using a 10 mm dense-macadam at 132° C (270° F). (3) A 6 mm even-textured macadam with an asphalt binder cutback with kerosene was shovelled into a wheelbarrow and applied to the road surface by shovel and spread by rakers. As before, further discussion of operation 3 is beyond the scope of this report.

These processes involved potential exposure to fumes, aerosols and particulate by inhalation. The substances could be derived from the bitumen and granite chips, as well as from the kerosene. Other substances, including PAHs, also were present in the diesel exhaust from the machinery used in the paving operations.

Results from personal sampling during road paving operations are shown in Table 3.11. In the paving processes, the chipper driver had the highest exposure to particulate matter, but

these particles contained little BSM. The authors did not analyze the BSM for PAH content, as was performed for tanker-truck loading (Section 3.1.3).
In addition, it was not clear what material was being indicated with the term "bitumen".

NAPA (1989) sampled workers' exposure to asphalt fumes during paving operations in Florida and Maryland. The operations at both sites involved placing a layer of hot-mix asphalt concrete on top of an existing asphalt pavement. The hot-mix was made from virgin asphalt cement and did not contain additives or recycled asphalt pavement.

Five workers at each location were fitted with personal sampling kits to monitor their occupational exposures. Details of the sampling and analysis techniques were as described for hot-mix handling and transport ( Section 3.2.5). The workers' positions were: paver operator, roller operator, two screedman, and a luteman (raker). Paving operations were fairly consistent during the workday in Florida. Paving operations in Maryland involved two separate sites. When the first site was complete, sampling was halted until paving operations began at the second site. The same filters were used for the full eight hours of monitoring in both studies.

The results presented in Tables 3.12 and 3.13 indicate that total exposures to asphalt fumes, consisting of particulate mass plus organic mass, were well below the recommended TLV of 5 $mg/m^3$ for all of the workers in both studies. Of the sampled fumes, the BSM was often a significant proportion. The gaseous hydrocarbons contained PAH concentrations an order of magnitude higher in the Florida samplings than in the Maryland samplings. This result is possibly related to the higher application temperature of the Florida hot-mixes, and to the application of twice the amount of asphalt material in the Florida paving operations than in the Maryland study. However, the total fume exposures were lower for the workers in Florida. Perhaps stronger coastal winds dispersed the fumes to a greater extent. In both studies, the paver operator received the greatest fume exposure, probably because his working location was in close proximity to the hot-mix material. The roller operator in the Florida study was frequently exposed to diesel exhausts in his breathing zone, which may have resulted in his particulate exposure being twice as great as those of the screedmen and luteman. Comparatively, the Maryland study indicated that the roller operator received particulate exposures similar to the screedman and luteman.

In all cases reported, the degree of exposure was below any published or known recommended standards.

## Asphalt Materials Testing

Testing of the physical and compositional characteristics of asphalt cements and asphalt concrete is performed through a variety of laboratory procedures. However, discussion of this topic is beyond the scope of this report. In addition, investigation of the literature has revealed no sources that pertain directly to the measurement of occupational exposure during asphalt materials testing. Three reports were identified regarding laboratory studies on the generation of fumes from paving-grade asphalt cements. For further information, the interested reader is referred to Eldridge et al. (1983), Brandt et al. (1985), and NAPA (1989).

## Asphalt Pavement Recycling

The reuse and recycling of deteriorated or distressed asphalt pavements is an economically attractive alternative to the direct disposal of used materials. This choice is due in part to asphalt's thermoplastic properties and high resistance to weathering and degradation. Some of the processes involved in recycling may increase the emission of pollutants to the environment.

When reclaimed asphalt pavement (RAP) is fed into a hot-mix asphalt concrete plant in the way that aggregate is normally processed (through direct contact with the burner flame), the material may become overheated. This would cause the asphalt to produce a visible blue smoke (The Asphalt Institute, 1983a). To remedy this problem, several innovations have been developed that introduce RAP into the hot-mix process through separate feed systems that heat the material by convection and to restrict the amount of RAP used in the paving mixture.

It should be noted that equipment used for in-place surface recycling operations, such as flame, microwave, etc., some may overheat the RAP and create significant quantities of asphalt emissions that are high in opacity. Investigation of the published literature has revealed no articles or reports concerning the monitoring or characterization of emissions generated by the use of RAP recycling.

## Exposure Biomonitoring

There has been a great amount of research on using short-term mutagenicity tests to assess human exposure to mutagenic and/or carcinogenic agents. These tests are typically applied to chemically complex materials, air contaminants present in working environments, and body fluids of exposed workers to evaluate the potential mutagenic and/or carcinogenic health hazards associated with occupational exposure to certain substances. In recent years, several investigations have employed such environmental and/or biological monitoring approaches in the study of workers exposed to asphalt fumes during hot-mix production and paving operations.

The following studies involving exposure biomonitoring refer to exposure of workers to asphalt and the hot-mix fumes during production and placement. Caution must be used in assessing the impact of these studies on the use of paving grade asphalt cements. The term "asphalt" again appears to be an all inclusive one covering coal tars, cokes and pitches as well as petroleum based asphalt cements.

The environmental monitoring approach typically includes several phases. Samples of the asphalt cement or hot-mix as well as personal and high-volume air samples of asphalt fumes are collected during construction operations. The material samples and high-volume air samples are analyzed for total PAH content and the personal air samples are analyzed for time-weighted-average (TWA) PAH content. The material samples and high-volume air samples also are assayed for mutagenicity by the Ames test (Ames et al., 1975).

The biological monitoring approach commonly involves the collection of urine samples from both occupationally exposed workers and non-exposed (control) subjects. Typically, these samples are commonly assayed for mutagenicity by the Yamasaki and Ames (1977) method. They may also be analyzed for the presence of thioethers and D-glucaric acid, which are products of the body's metabolic detoxification systems (Chapter 2). Urinary thioethers provide a nonspecific index of exposure to electrophilic compounds that conjugate with glutathione. D-glucaric acid signals exposure to compounds that induce microsomal enzyme function. Thus, monitoring these substances can indicate exposure to PAHs and the body's capacity to detoxify and expel them. Because tobacco smoke contains significant PAH contents, biological monitoring data often are analyzed with respect to a subject's smoking habits.

Sforzolini et al. (1986) combined environmental and biological monitoring approaches to study three Italian working environments exposed to petroleum derivatives, including the process of paving with asphalt hot-mix. The environmental monitoring approach involved assaying the asphalt for PAH content and mutagenic activity, and sampling the asphalt fumes and analyzing them for total and TWA PAH concentrations and for mutagenic activity. The biological monitoring plan involved collection and examination of urine samples from exposed and control workers. The urine was assayed for mutagenicity, both before and after work, and D-glucaric acid and thioether excretion were also monitored. Confounding factors, such as smoking habits, alcohol consumption and medicine use were identified with a questionnaire.

Both the environmental and biological monitoring results are given in Table 3.14. The total PAH and BaP contents in the asphalt samples were typical (Chapter 2) and the asphalt fume and PAH exposures were low. Both the asphalt material and fume samples also were found to be nonmutagenic. Urine mutagenicity was detected with bacteria and by metabolic activation; beta-glucuronidase did not increase mutagenicity. However, occupational exposure was not indicative of mutagenicity, while the effect of smoking on this parameter was substantial. Analysis of D-glucaric acid showed that its excretion was higher only among smoking subjects of both groups and occupational exposure was of no influence. In addition, thioether excretion did not appear to be influenced by smoking or occupational exposure.

The authors concluded from these results, as well as results from the other two environments studied (exposure to mineral oils and to petroleum coke and pitch), that a correlation exists between PAH content and mutagenicity in raw materials and air samples, and between the environmental data and urine mutagenicity in exposed workers. It could also be concluded that in this study occupational exposure did not adversely affect the workers.

Monarco et al. (1987) and Pasquini et al. (1989a) combined environmental and biological monitoring techniques to study occupational exposure to asphalt fumes during road paving operations in Italy. The study population consisted of 17 male workers (5 paving machine operators and 12 screed operators) who were divided into three team groups. Each group processed about 500 tons of asphalt hot-mix per day with an exposure time of 4 to 6 hours/day. The screed operators were mainly exposed to asphalt fumes, while the paver operators showed a mixed exposure to asphalt fumes and diesel exhaust.

One sample of hot-mix was collected during paving operations by each group, totaling 3 samples. The asphalt was removed from the mixtures, the asphaltenes separated, and the remainder submitted to extraction with dimethylsulfoxide (DMSO), which concentrates mainly PAHs. The DMSO extracts were then analyzed for PAH content and assayed for mutagenicity. PAHs were measured at levels typical among penetration-grade asphalts (Table 3.15) and the extracts were found to be nonmutagenic with two strains of bacteria and with or without metabolic activation (Table 3.16).

All workers were monitored for occupational exposure to asphalt fumes. The mean TWA values, $\pm$ SD, (paver operators 0.58 $\pm$ 0.25 $mg/m^3$, screed operators 0.83 $\pm$ 0.63 $mg/m^3$) were well below the TLV (5 $mg/m^3$) and the organic contents of the airborne particulate (measured as cyclohexane-soluble matter) were not substantial (paver drivers 0.17 $\pm$ 0.05 $mg/m^3$, screed operators 0.16 $\pm$ 0.12 $mg/m^3$).

High-volume air sampling also showed 0.54 $mg/m^3$ asphalt fumes for consecutive sampling ($S_1$) and 3.67 $mg/m^3$ for sampling only during paving operations (Table 3.17). Ethyl ether extracts from these airborne particulate detected PAH contents (Table 3.17) that were qualitatively similar to the material samples. Mutagenic activity was absent in both air samples in all doses tested with two bacteria strains, with or without metabolic activation (Table 3.18).

For biological monitoring, the 17 exposed workers were compared to 27 unexposed male office clerks. Two urine samples were collected from each subject at the end of the working week: the first upon waking in the morning, and the second at the end of the day (about 16 waking hours). Results were analyzed after dividing the subjects into four groups to determine the contributions from both smoking and asphalt exposure to the urinary parameters.

From exposed non-smoker subjects, 82% of urine samples were mutagenic; a significant difference over unexposed non-smokers (Table 3.19). Among non-smokers, exposed workers also had higher mutagenicity per 100 ml urine in all day samples than controls (Table 3.20). These differences were still significant when the values were corrected for creatinine excretion. Among smokers, urine mutagenicity was always present due to cigarette smoke exposure. Among controls, the mutagenicity was statistically higher in smokers than non-smokers. These findings appear to indicate that: a) smoking is a major confounding factor in urine mutagenicity, and b) even though the measured asphalt fume concentration was very low, asphalt exposure may have a more significant impact on urine mutagenicity when the smoking factor is present.

Among non-smokers, urinary thioether excretion was slightly higher in exposed than in unexposed subjects (Table 3.21). Similar results were seen among smokers. Neither of these differences were statistically significant. However, when comparing exposed smokers to unexposed non-smokers, the difference was significant ($P<0.002$). This finding could be due to a synergistic effect of the combined exposures to asphalt fumes and cigarette smoke.

The excretion of D-glucaric acid was not significantly affected by asphalt exposure or smoking habits (Table 3.22). This result indicates that exposure to compounds that induce MFO activation was not sufficiently high in either asphalt fumes or cigarette smoke so as to increase D-glucaric acid excretion.

The biological monitoring approach using urinary mutagenicity assays suggested a presumptive exposure to indirect-acting mutagens which were not discovered using environmental data collected during paving operations with asphalt hot-mix. Therefore, the authors conducted additional *in vivo* experiments to evaluate urinary excretion of mutagens in laboratory animals treated with the DMSO extract of the sampled hot-mixes (Pasquini et al., 1989b).

The *in vivo* experiments involved intraperitoneal injections into rats of the DMSO extract dissolved in olive oil. The animals were killed at fixed times and their livers removed and processed for analysis. This organ was chosen because it contains considerable MFO activity (Chapter 2). In fact, the hepatic enzyme system is generally considered the most appropriate for the metabolic activation of procarcinogens, including PAHs (Pelkonen, 1976).

Similar to the *in vitro* assay using the Ames test, the *in vivo* assay did not reveal any mutagenic activity. The authors noted, however, that the nongenotoxic effect in the liver does not exclude eventual DNA damage in other target organs (e.g., lung, kidney, or bladder).

In a short communication, Lafuente and Mallol (1987) presented results from a preliminary study on the biological monitoring of Spanish asphalt workers. The study involved monitoring urinary thioether excretion in six workers: four in paving and two in hot-mix production. Urine samples were collected from each subject on four days during one week, including a nonworking day (Sunday). One of the subjects also was monitored daily for three weeks; he worked only the first two weeks and was not in contact with asphalt for the third week. All samples were taken at the end of the day.

The results (not reported) showed an unusual pattern. Urinary thioether excretion increased during the first days of the working period and decreased during the last days of the week. This pattern was evident in all of the subjects. It was especially clear in the three-week study and during the rest period (week 3) thioether excretion remained roughly constant. Maximum values were obtained from Tuesday to Thursday (6-24 mmol SH/mol creatinine), whereas minimum values were obtained from Friday to Sunday (1-2 mmol SH/mol creatinine).

It is well known that urinary thioethers increase during exposure to electrophilic compounds, and that this increase is clearly related to the degree of exposure (Van Doorn et al., 1981). Four subjects were heavy smokers, which could have contributed to the increase of thioethers, but this factor cannot explain the biphasic pattern observed because the number of cigarettes consumed each day was reported to be constant. Lafuente and Mallol (1986) demonstrated that urinary thioether excretion remained roughly constant when the smoking habit is constant. Additionally, nonsmoking subjects presented the same excretion pattern as the smokers. Therefore, the authors considered the biphasic pattern to be associated only with asphalt exposure.

Within the biphasic excretion pattern, the initial increase was probably due to electrophilic compounds in the asphalt emissions and to their conversion into nontoxic GSH conjugates. However, the subsequent decreases cannot be explained by a decrease in the contamination process, since the exposure was essentially the same each day, and since no differences were found between the paving workers and the workers in hot-mix production. The authors suggested that either the body's GSH contents are exhausted after the first days of exposure or that there exists some are chemical components that can inhibit GST activity. Both cases have been described in the literature (Hayakawa et al., 1975; Van Doorn et al., 1980). The three-week study indicated that after two non-exposed days, GST activity and/or GSH contents was restored.

Burgaz et al. (1988) examined urinary thioether excretion among Turkish workers exposed to asphalt fumes during hot-mix production and paving operations. The exposed workers consisted of 12 men working in hot-mix production (Group A) and 32 men working on paving operations (Group B). These subjects were compared to an occupationally non-exposed group of 37 male office clerks (Group C). Details of the subjects' smoking habits and usage of medication were given in the article. Urine samples from exposed subjects were collected at the end of an 8-hour work day on Thursday or Friday. Samples from the controls were collected at different times of the afternoon or evening, whenever convenient.

Results of the urine analyses are summarized in Table 3.23. Mean thioether excretion in the exposed groups was slightly and consistently higher than in the controls, but the differences were not statistically significant. Exposed nonsmokers did not differ from control nonsmokers. In contrast, thioether excretions of exposed smokers were significantly higher than those of control smokers. The authors suggested that a difference in smoking behavior may have resulted in this finding. Smoking data indicated that the exposed groups did contain more heavy smokers than the control group. The authors also reported that the mean values for exposed (A and B) and control smokers were significantly higher than the mean values respectively for nonsmoking exposed ($P < 0.025$, $P < 0.005$) and control workers ($P < 0.025$). These results suggest that smoking was responsible for the majority of thioether excretion.

No significant differences were found between subjects receiving medication and those not receiving any medication. This finding suggests that taking medicine should not be regarded as a decisive factor in increased thioether excretion.

Another approach to occupational biomonitoring, which differs from those reviewed previously, involves the presence of lung constituents in sputa. The major proportion of cellular components found in most of the sputa from persons working in polluted atmospheres usually are alveolar macrophages. The free alveolar macrophage is the main defense system of the respiratory tract against damage from airborne dust and other particles, such as aerosols and bacteria, and also from toxic gases. It is presumed that alveolar macrophages phagocytize such foreign material, as well as dead cells or cell components and surfactants from the lung. To a slight degree, they are capable of replicating themselves, but their main source is the blood monocytes, which become transformed into alveolar macrophages in the lung tissue. The number of alveolar macrophages present is consequently a reflection of the reaction of the lung tissue to air pollution. Thus, counts of alveolar macrophages present in smears made of sputa from exposed workers probably reflect the lung reaction to air pollution.

Mylius and Gullvag (1986) investigated this phenomenon by using the sputa of Norwegian workers from several different types of industries. The authors performed a pilot investigation on paving with asphalt. Thirty-one asphalt workers were compared to 36 university students and teachers in a control group. Subjects were required to cough vigorously, and the produced sputa was made into eight smears. The smears were viewed under a microscope and the number of macrophages present in a single field across the middle of the smear was counted. The mean alveolar macrophage value for all eight slides of each sample was then calculated for comparison.

The results (not shown) indicated a slightly greater difference in alveolar macrophage count between exposed nonsmokers and control nonsmokers than between control smokers and control nonsmokers. A dramatic increase was observed among exposed smokers compared to non-exposed smokers. This finding suggests a strong synergistic effect on lung reaction when occupational exposure to asphalt fumes is combined with tobacco smoking. It also shows that the alveolar macrophage test of pollutant levels is sensitive, since increased counts over the controls were observed in all of the asphalt workers, who spend most of their work time in open air and are typically exposed to low concentrations of asphalt fumes.

## Discussion

Presented in this chapter are reviews of the identifiable investigations concerning occupational exposure to emissions from the use of petroleum asphalt in the paving industry. Essentially, these studies attempt to (a) identify the physical character of asphalt fumes, (b) estimate atmospheric concentrations and respiratory exposure to these fumes, and (c) relate the observed biological responses in workers to a measure of the exposure to mutagenic and/or carcinogenic agents in the fumes.

In America, OSHA (1988) proposed to regulate occupational exposures to asphalt fumes to an 8-hour TWA concentration of 5 $mg/m^3$. Several other nations have established similar standards as guidelines or regulations. These standards are vague, however, because the term "asphalt fumes" is very general. Asphalt fumes are complex mixtures of organic and inorganic matter. The organic matter is composed of various hydrocarbons. It exists in the fumes as a gas or vapor as well as adsorbed to the inorganic matter, which is composed of mineral particulate. Because it is a complex mixture, a given emission of asphalt fumes can be measured at various concentrations depending on the sampling and analytical techniques employed. In addition, the term "asphalt" does not always mean petroleum asphalt but, in many other countries may also refer to coal tars or pitches.

The identifiable reports on emission sampling provide only a few estimates of the character and magnitude of asphalt fumes and direct respiratory exposures to paving workers. These reports also provide no applicable information on direct exposure to the skin. In addition, some of the studies included factors that may confound exposure assessments. These factors include: (1) inconsistencies in sampling and analysis procedures among investigators and (2) the concurrent sampling of extraneous matter emitted from various external sources. Hence, the available physical sampling data do not represent a broad spectrum of information regarding direct human exposure through occupations using paving-grade asphalt cements or hot-mix asphalt concrete production or placement.

The available information does suggest several important points concerning occupational exposure:

(1) Occupational exposures to workers commonly fell below a value of 5 $mg/m^3$.

(2) Particulate matter usually comprised the predominant material sampled in personal respiratory monitoring.

(3) Based on only one study, the predominant sizes of particulate sampled during the monitoring of industry processes may at times occur within the respirable size range (i.e., less than 10$\mu$m) as defined by Sanders (1986).

(4) The organic fraction (material soluble in low molecular weight hydrocarbons) of sampled particulate matter varied widely (less than 10% to greater than 50%) among different duties involved in the paving industry.

(5) Processes involving physical transference of the asphaltic materials (e.g., truck loading or feeding hot-mix through the paver) typically produced greater emissions than other processes (e.g., hot-mix compaction).

(6) Polynuclear aromatic hydrocarbons in some forms and to different extents were common to all of the analyses that measured the character of the emissions

(7) Sampling and analysis procedures may have had a significant effect on measured concentrations of substances.

The few biomonitoring studies presented in this chapter involved both environmental and biological monitoring of occupational exposures to asphalt fumes from hot-mix preparation and paving operations. Environmental monitoring typically found that the concentrations of fumes and the PAH contents of fumes and asphalts were in agreement with previously reported values (Chapters 2 and 3). When tested for bacterial mutagenicity, these materials always tested negative. Biological monitoring involved analyzing urine samples for bacterial mutagenicity and for the presence of thioethers and D-glucaric acid, which are produced in response to significant exposure to compounds such as PAHs. One study also measured lung reaction to asphalt fume exposure by observing the presence of alveolar macrophages in sputum samples. The biomonitoring results generally showed negative urine mutagenicity and contradictory urinary excretions. However, the studies did show that tobacco smoking was a major confounding factor and that biological reactions increased synergistically with dual exposure to smoking and asphalt fumes.

## Summary

The identifiable reports concerning occupational exposure to asphalt emissions cover a wide range of processes in the paving industry but are lacking in pertinent identification and quantity. Emissions sampling data provide only a few approximations of atmospheric concentrations of asphalt fumes and respiratory exposure to these fumes. The data do suggest that occupational exposure to asphalt fumes commonly falls below 5 $mg/m^3$. Biomonitoring data also are limited, and the results are sometimes contradictory. However, these data do suggest that (a) tobacco smoking is a major confounding factor in biological monitoring, and, (b) synergistic biological reactions occur when smoking is combined with exposure to asphalt fumes.

# Chapter 4 Health Effects

This chapter discusses the identifiable sources concerning health effects potentially associated with exposure to paving-grade asphalt cements used in hot-mix asphalt paving operations. These sources include: (1) case reports and epidemiological studies of health effects in humans following occupational and environmental exposures, and (2) laboratory studies of health effects in experimental animals following controlled exposures by different routes. The health aspects of asphalts (or bitumens) have been reviewed previously by NIOSH (1977), Bingham et al. (1979), Bright et al. (1982), King et al. (1984), IARC (1985), NAPA (1985), and Santodonato (1985).

## Human Health

Health studies on humans can provide valuable information for the direct evaluation of potential health risks in man. This section contains reviews of the identifiable literature regarding human health effects from exposure to asphalts used in hot-mix asphalt pavement construction. These sources include reports of health effects in individuals, occupational cohorts, and the general public.

## Case Reports

Case reports provide information on individual cases of health effects and potential associations with exposure history. Only one case report has been identified from the literature. Guardascione and Cagetti (1962) reported a case of laryngeal cancer in a worker employed in road bituminization which was a mixture of asphalt, coal tar and pitch. This report recognizes the problems with coal tars but they are not a subject for this study.

## Epidemiological Studies

Epidemiology is the study of the occurrence of health effects in man. In epidemiology, focus is placed on patterns and determinants of health effects in groups of people such as occupational cohorts, rather than on diagnosis and treatment of individual effects. Study designs commonly encountered in epidemiological investigations include a) the uncontrolled case study, b) the cross-sectional study, and c) the proportional mortality (or morbidity) study. (Wright, 1983).

Uncontrolled case studies are the simplest of occupational studies. They report the occurrence of an unusual number of health related effects among a group of people. Typically these studies provide only qualitative exposure estimates and no quantified rates of occurrence. Investigation of the literature has revealed no such studies related directly to hot-mix asphalt concrete.

Cross-sectional studies survey the prevalence of health related effects in groups of people and the potential relation to current or past exposures to substances. These studies can be used to identify particular causal agents of health effects, however, interpretation of the results must often be limited due to the introduction of biases. Sources of bias may include the incomplete accounting of all cases of a health related effect or concomitant exposures leading to the effect. These studies may not identify the time sequences necessary to establish causal relationships and do not provide incidence data.

Henry (1947) correlated occupations and suspected causative agents with 3,753 cases of skin cancer in 2975 persons reported to the Chief Inspector of Factories in Britain between 1920 and 1945. These cases were reported under the Workmen's Compensation Act by the definition "Epitheliomatous ulceration or cancer of the skin due to pitch, tar, bitumen, paraffin or mineral oil or any compound or residue of any of these substances or any product thereof contracted in a factory or workshop."

Henry's investigation yielded 22 cases in 21 workers employed in road construction; 13 cases in 12 persons who applied road surface materials and 9 in workers who made macadam pavements, known to the author as "asphalt." Most of these persons worked with coal tars, but Henry attributed one cancer case solely to bitumen (asphalt) exposure. This case involved a facial epithelioma on a worker who had been employed for 23 years at a lake asphalt works where only "bitumen" was used. This material was mainly a natural product from the Trinidad Lake, but occasionally it was produced artificially from a mineral oil. Further details were not reported.

DeMent et al. (1987) reported six cases of primary lymphomas of the liver and reviewed the published literature on this topic. The authors identified 22 previously reported cases confined to the liver and others that were presumed to be primary to that organ, but could not be confirmed. Occupational exposures were not detailed in the previously reported cases.

Of the six cases reported by the authors, four individuals were employed in occupations where exposure to PAHs from fossil fuels occurred. One of these four was a 62-year-old white male who had been employed as a liquid asphalt sprayer for 30 years. Further details of this man's exposure history were not reported. The final diagnosis indicated that the tumor was a diffuse large cell lymphoma of B-cell phenotype.

Several other reports have been identified that involve incidences of cancer of the lung (Vineis et al., 1988; Menck and Henderson, 1976; Blot and Fraumeni, Jr., 1976; Pastorino et al., 1984), bladder (Howe et al., 1980; Mommsen and Aagard, 1984; Risch et al., 1988), liver (Austin et al., 1987), and renal pelvis (McLaughlin et al., 1983; Jensen et al., 1988). These studies only show elevated cancer risks in workers exposed to various bituminous products without clear definition to their source. They do not provide information regarding incidences of health related effects associated solely with exposure to paving asphalts.

In a related study, Baylor and Weaver (1968) conducted a health survey of workers in several occupations that involved exposure to petroleum asphalt. As part of the survey, seven petroleum companies that produced asphalt provided information on workers from 25 oil refineries. A study group consisted of 462 employees with five or more years of work with asphalt and a control group consisted of 379 other refinery workers. The average work experience of these employees was 15.1 years. A medical assessment was conducted on every worker in each group. The assessments included detailed review of the worker's occupational and medical histories and a brief physical examination with emphasis on the skin and respiratory tract (Table 4.1).

A summary of the medical histories revealed few cases of cancer; one control worker died of lung cancer at age 65, another control reported a carcinoma of the colon, one asphalt worker had a carcinoma of the stomach, and skin cancer (basal cell epithelioma) was reported in four controls and two asphalt workers. At the time of the survey, skin cancer also was present in four asphalt workers, however two of them had cancer prior to beginning work in asphalt operations.

Past lung disease other than cancer was reported in 31 of 360 asphalt workers (8.6%) and 12 of 277 controls (4.3%). The majority of these cases were chronic bronchitis while a few workers had asthma or emphysema. None of these illnesses were described as advanced, severe, or incapacitating, and several were diagnosed solely on the basis of "increased bronchial markings" on the chest x-ray film. At the time of the survey, miscellaneous lung disease was noted in 40 of 462 asphalt workers (8.6%) and in 24 of 379 controls (6.3%). No case in either group was described as severe or incapacitating.

The medical histories reported instances of noncarcinogenic skin disease in 37 of 360 asphalt workers (10.3%) and in 47 of 277 controls (17%). During the physical examination, 26 of 462 asphalt workers (5.6%) and 20 of 379 control workers (5.3%) were found to have skin diseases. These cases consisted mainly of localized and transitory dermatitis and none were considered extensive or severe.

Other health problems discovered during the physical examination included hypertension in 27 asphalt workers (5.8%) and 27 control workers (7.1%), peptic ulcers in 12 asphalt (2.6%) and 8 control workers (2.1%), heart disease in 17 asphalt (3.7%) and 14 control workers (3.7%), and other miscellaneous disorders paralleling what would be expected in the general population. Incidental findings indicated that the most serious threats to the health of both the asphalt and the control workers were in the petroleum industry were obesity and heavy cigarette smoking.

In addition to the refinery survey, Baylor and Weaver (1968) conducted a survey of employees in the highway construction, roofing, and trucking industries. This information was obtained by means of a questionnaire from company and insurance reports and from State Highway Commissions and Boards of Health. The authors noted that this information may not be highly reliable.

Among the 31 construction or paving companies that responded, only one case of transitory nasal irritation and 14 cases of dermatitis were reported as resulting from the 11,478 man-years of exposure to asphalt. Three large roofing companies reported no ill health attributable to asphalt in their more than 1,100 asphalt workers. Four trucking companies employing more than 5,000 drivers reported no known cases of skin or lung disease attributable to asphalt fumes or dust from asphalt-paved roads. Of six insurance carriers responding to the questionnaire, only one reported any claims involving asphalt. These included one case of headache, one case of silicosis secondary to asphalt, one case of leukoplakia, and one case of dermatitis secondary to asphalt. One insurance company, which serviced over 43 companies whose primary business was asphalt production or use, reported no known cases of compensation involving occupational exposure to asphalt.

Baylor and Weaver concluded that petroleum asphalt cannot rationally be considered a hazardous substance. They did note, however, that asphalt may cause some individuals, depending on the extent of exposure, to be subject to some form of health problems prompted by contact with it or its components.

A publication of the National Center for Health Statistics (Wilder, 1973) was used by NIOSH (1977) as a comparison to the data obtained by Baylor and Weaver. Wilder reported a combined incidence of chronic bronchitis, emphysema and asthma of 11.8% for males, 16 to 65 years old, in the "usually working" category. The comparison of this value with those from the asphalt exposed workers yielded relative risk values which were not significantly different by the normal-deviate test. Information concerning lung disease other than cancer indicated a relative risk for asphalt workers compared to control workers that was only significant at the less than 5% confidence level. The relative risk for current lung disease also was not significantly different for the two groups or the for the U. S. working population as a whole (NIOSH, 1977). The NIOSH authors concluded that quantitative evaluation of the report by Baylor and Weaver was not possible because of the lack of detailed results and exposure data, however, they did state that the authors' conclusion that the asphalt workers studied were not under an appreciably greater hazard than the controls was reasonable on the basis of the statistics reported.

Proportional mortality studies measure the proportion of deaths in a group of people, due to specific causes, compared to deaths from a general population. Similarly, proportional morbidity studies measure the proportional incidence of diseases in a group of people. Investigation of the literature has revealed no such studies involving occupational cohorts exposed solely to asphalt emissions through paving operations. However, the following studies are presented to indicate potential areas that can be confused with the effects asphalt cement.

Maizlish et al. (1988) investigated mortality among highway workers in California, U.S.A. The study population was defined as all California Department of Transportation (CalTRANS) employees who left employment for any reason and who died in California between 1970 and 1983, inclusive. Statistical analyses were performed on 1,570 total deaths and including a subgroup of 327 decedents (21%) with a last job in highway maintenance. Maintenance personnel continually work with a variety of substances, including asphalt. The report by the CalTRANS officials substantiated this with their report that highway maintenance workers had the greatest potential for exposure to chemical hazards, including asphalt, in pavement and roadside maintenance (Table 4.2).

Standardized proportional mortality ratios (PMRs) were calculated relative to proportional mortalities for the United States population through 1980. Results of the analyses are presented in Table 4.3. Regarding health effects among the highway maintenance workers, there was a statistically significant excess of deaths only from emphysema (PMR=250). A significant deficit of deaths due to circulatory disease (PMR=83) also was observed.

The authors noted several factors that confound the etiological significance of this investigation. Some of which are (1) Because highway maintenance typically requires some strenuous activity, the healthy worker effect may have understated the calculated risks (i.e., PMRs), (2) Data on cigarette or alcohol consumption were not available for the study group, so the PMRs could not be adjusted for these factors. Therefore, the potential health risks of this cohort may be overestimated, particularly with regard to (a) lung cancer and emphysema, which are associated with cigarette smoking (Surgeon General, 1982), and (b) cirrhosis of the liver, which are associated with excessive alcohol consumption (Berkelman et al., 1986), and (3) Classification of the workers based only on their last job may have misclassified their exposures, depending on many factors. These factors include the lack of (a) occupational exposure data, (b) histories of work-type and job mobility, (c) knowledge of previous or concomitant non-CalTRANS occupations, and (d) non-occupational exposure data including knowledge of recreational risk factors.

Bender et al. (1989) and Parker et al. (1989) recently investigated cancer and noncancer mortality among highway maintenance workers (HMWs) in Minnesota, U.S.A. The study cohort consisted of 4,849 men with 1 or more years of experience as a HMW for the Minnesota Department of Transportation (MNDOT) and who had worked at least one day from 1945 to 1984. Duties of the HMWs included the upkeep of highways (repairing road surfaces, sealing joints, maintaining shoulders, and repairing and improving drainage structures), traffic services (sanding roads and removal of ice and snow), and other maintenance operations (construction and maintenance of road signs and traffic markers, weed control, and general maintenance of the right-of-way). This cohort contained workers who were exposed to paving asphalts as well as to other substances, such as those shown in Table 4.2.

The expected number of deaths in the HMW cohort was calculated using a comparison population of white male Minnesotans. Standardized mortality ratios were then calculated to demonstrate the observed health risks. Due to important urban/rural differences in cancer and noncancer mortality rates, both the HMW cohort and comparison populations also were divided into urban and rural subpopulations. Approximately one-third of the study cohort was urban and two-thirds were rural (Table 4.4). Rural workers tended to start work at the MNDOT at an older age and work for the MNDOT longer than their urban counterparts. The largest number of workers entered the cohort during the 1950s and 1960s and between their 20th and 30th birthdays. The 4,849 workers in the cohort contributed 96,567 person-years to this study.

Results for selected cancer and noncancer mortality among the study cohort are presented in Tables 4.5 and 4.6, respectively. Based on 1,530 deaths in the cohort, a statistically significant deficit was observed for deaths from all causes. The reduced mortality experience was independent of the number of years worked, latency, and decade of hire. All three major causes of death contributed to this deficit: cancer (18%), circulatory diseases (57%), and cerebrovascular disease (8.5%). The authors cited the healthy-worker effect as a strong influence on the deficit and they noted that incomplete or inaccurate follow-up was unlikely to be a source of bias.

For cancer-related mortality, the reduced SMR for all cancers was statistically significant. The major contributor to this deficit was the significant reduction in lung cancer, which is strongly suggestive of decreased cigarette smoking in the HMW cohort. This interpretation is inconsistent, however, with the SMRs for other smoking-related causes of death, which were nominal and not indicative of decreased smoking experience. These other causes include chronic bronchitis, emphysema, chronic obstructive pulmonary disease, cancer of the mouth and pharynx, and kidney and bladder cancers.

The two major contributors to the deficit in all circulatory diseases were ischemic heart disease and cerebrovascular diseases. There were no significant differences in overall cardiovascular mortality or in the specific subcategories between urban and rural workers, and there were no trends in mortality when examined by duration of work, year of hire, or latency.

The authors noted that the MNDOT had been collecting solvent-exposure data during asphalt paving operations for five years. All exposures were reported to be well below the threshold limit value for petroleum distillates, xylene, benzene, hexane, and toluene. Analysis of bulk samples of asphalts, oils and tack coats currently used by the Minnesota HMWs, as well as breathing zone samples, failed to detect pyrene, benzo[a]pyrene, or chrysene. Therefore, current HMW exposures to these agents may be minimal, but current exposures provide no basis for inference about historical exposures to them. Additional efforts were noted to be underway to further characterize HMW's exposure to asphalt.

## Animal Studies

Laboratory studies on experimental animals serve as a second primary but many times highly inadequate means of establishing information on the potential adverse health related effects associated with exposure to asphalts. The procedure for conducting the studies are highly artificial and can be misleading. This section reviews the identifiable studies involving the exposure of animals to paving-grade asphalt cements. The primary routes of exposure to the animals consisted of repeated applications to the skin and injections under the skin or into muscle tissue. Other studies on asphalt fumes also are discussed. These studies are informative but the limitations and parameters must be well defined.

## Dermal Application Experiments

Most common of the animal toxicological experiments pertinent to this study are those that involve skin applications of asphalt. Simmers et al. (1959) assessed the dermal carcinogenic potential of a mixture of steam-refined and air-blown asphalts from six different samples supplied by southern California refineries. The asphalts were pooled for this experiment, and a portion of this pooled sample was mixed with sufficient benzene to make it fluid enough to be painted on the skins of animals. The proportion of benzene was not reported.

Two groups of mice were used for the skin painting study. In the asphalt-exposed test group, which consisted of 32 male and 36 female mice, the asphalt-benzene mixture was applied to the skin of the interscapular region twice weekly with a glass stirring rod. A control group of 31 male and 32 female mice was treated similarly, but with benzene alone. The exposure concentrations of asphalt or benzene were not reported for either group.

Results among the mice in the test group included loss of hair, dryness and scaling of the skin, and formation of papillomas at the painting sites. The authors also reported 12 epidermoid carcinomas on the test mice, the first of which appeared 54 weeks after initiation of treatment. These cancers were judged to be malignant based on their microscopic form and structure, but no metastic lesions were reported.

The authors' method of reporting these cancers as the total number of malignant growths leads to confusion about the number of mice with such growths. The tone of the discussion tends to imply one growth per mouse. Simmers provides additional information about the results in the introduction to a subsequent paper (Simmers, 1965a) where he reported 22% of the mice coming to autopsy eventually developed epidermoid cancers. With this information, the number of autopsied mice can be adjusted to 54 or 55 animals.

Results among the control mice consisted mainly of hair loss and dry and scaling skin, similar to the asphalt-exposed animals. However, no papillomas or epidermoid cancers occurred in the control group although the authors reported that microscopic investigation of the organs of one animal that died during the study disclosed leukemic infiltration of the lungs and the salivary glands.

Simmers et al.(1959) concluded that the tested asphalts contained substances that will cause epidermoid carcinomas when applied externally to the skin of mice. However, they did not establish a dose-response relationship for the asphalts. The authors also did not address the cocarcinogenic potential of the benzene diluted media. Benzene is widely suspected as a potential leukemogen (Vigliani, 1976) which may explain the case of leukemic infiltration, but data is lacking on benzene's cocarcinogenic potential.

Because of the possibility that benzene may have acted as a cocarcinogen in his previous painting study, Simmers (1965a) conducted another study that was designed to test the carcinogenicity of asphalts that had not been mixed with a diluent. Another goal of this study was to determine whether air-refined and steam-refined asphalts differed in their carcinogenic potency. For each asphalt type, a pooled mixture of three samples refined from a west coast crude was formed and analyzed by generic compound class. The steam-refined asphalts contained 24% asphaltenes, 31% aromatics (naphthene aromatics), 33% resins (polar aromatics), and 12% saturates. They differed substantially from the air-refined asphalts which contained 41% asphaltenes, 26% aromatics, 22% resins, and 11% saturates.

Twenty-five male and 25 female mice, approximately 6 weeks old, were painted with air-refined asphalt 1 to 3 times a week, depending on skin condition. A similar group of mice was painted with steam-refined asphalt 3 times per week. No controls were reported for either group. Before the paintings began, the hair over the scapular region of all of the mice was closely clipped. To facilitated application, each asphalt was softened by heating its container in boiling water. Approximately 75 to 100 mg of asphalt was applied with a glass rod at each painting. At the time of application the asphalt had cooled, but its temperature was not determined.

After 7 weeks, 32 animals (14 males and 18 females) (64%) from the air-refined group survived an epidemic of pneumonitis to continue the experiment. The number of paintings for the remaining animals ranged from 22 for an animal that died after 63 days to 270 for a mouse that was killed after 21 months and 23 days. Simmers noted that the air-refined asphalt hardened to a plaque which the animals frequently pulled off, tearing the skin. Autopsies showed one papilloma and one tumor of skin accessory structure origin, each at the site of asphalt application, and one adenoma of the lung. The usual pathological change at the painting site was chronic dermatitis. No carcinomas were reported from this group.

From the steam-refined asphalt group, 27 animals (15 males and 12 females)(54%) survived the epidemic. After one year of treatment, one male and five females were alive and all were showing skin reactions. Causes of mortality for the other animals were not reported, although they also showed unspecified skin reactions to the asphalt. This response prompted the addition of 8 male and 5 female mice to this group to complete the study. The number of paintings for the animals coming to autopsy ranged from 16 to 240. Of these animals, three developed epidermoid carcinomas at the site of application, one of which was of skin accessory structure origin. Two papillomas also were found in this group.

Simmers (1965a) observed that neither of the undiluted asphalts made good contact with the skin, particularly the air-refined asphalt. Therefore, he conducted another set of experiments for the study using air-refined asphalt diluted with toluene in a ratio of 10 to 1. Ten male and 10 female mice were painted with this mixture 3 times a week for 2 years. The applications totaled 284 with approximately 20 to 30 milligrams per application. To maintain the paintable consistency of the mixture, toluene had to be added periodically because of its rapid evaporation. An exact determination of the asphalt concentration was not possible because of this evaporation and repeated addition of solvent. As a control group, 5 male and 10 female mice received applications of toluene alone 3 times a week for 19 months for a total of 230 applications. Simmers did not estimate the amount of toluene applied because of its rapid evaporation.

Autopsies on the asphalt-toluene group showed 9 epidermoid cancers of the skin, including one of skin accessory structure origin in an animal painted 147 times. One epidermoid cancer in an animal painted 240 times had invaded a regional lymph node and virtually replaced the lymphoid cells. Another animal painted 252 times developed an epidermoid carcinoma that had invaded the scapula. Two lung adenomas were observed in other animals. In two animals, the only abnormal condition observed was chronic dermatitis.

Eight of the 15 toluene controls were autopsied and 6 examined microscopically. One of these mice had a small papilloma and others showed loss of hair, scaling, and thickening of the epidermis and dermis. A summary of all results is given in Table 4.7.

In discussing the results, Simmers noted that the low yield of cancers from the experiments with pure asphalt was striking when contrasted with the much higher yield from the toluene-diluted asphalt experiment. He suggested that this difference related to the ability of the asphalts to maintain intimate contact with the skin. This reasoning also is supported by the higher cancer yield from steam-refined asphalt, whose lower viscosity and melting temperature allowed it to achieve better skin contact than the air-refined asphalt.

Simmers also noted a possible complication in the results. Close examination of the toluene diluent detected the presence of contaminants as indicated by a faint fluorescence in ultraviolet light. Although fluorescence does not prove that the contaminant is carcinogenic, the high incidence of cancer in the asphalt-toluene treated mice and the skin changes in the toluene controls suggests the possibility of cocarcinogenic effects.

Because of the chemical complexity of asphalt, Simmers (1965b) studied the carcinogenic potential of generic compound classes in asphalt. A sample of steam-refined asphalt derived from California crude petroleum was separated into four classes of compounds: asphaltenes, aromatics, saturates and resins. Because of the association between ultraviolet fluorescence and the carcinogenicity of hydrocarbons, Simmers decided that these fractions were most likely to contain the most potent cancer producing compounds.
Twenty-five males and 25 female mice were treated with a pooled mixture of the aromatic and saturate fractions of the asphalt. The material was rubbed into the fur of the interscapular area 3 times a week with a glass rod for a minimum of 72 and a maximum of

242 paintings. The amount of material applied was estimated at 33.4 mg per painting. No controls were used in this study.

Results from the experiments are shown in Table 4.8. Forty of the original 50 animals came to autopsy, but 10 of these were not examined microscopically because they showed no gross evidence of neoplastic formations. Eleven animals survived the maximum number of paintings. Complete hair loss, along with dry and scaly skin, was a consistent finding in all animals. Thirteen of the 30 mice studied microscopically had cancers that included 7 epidermoid carcinomas, 5 basal cell or baso-squamous cancers, and one cancer of probable sebaceous gland origin. Thirteen well defined papillomas also were seen. Underlying a papilloma on one animal was a leiomyosarcoma. Another had an epidermoid carcinoma that had metastasized to the lung. An animal with an epidermoid carcinoma of the anus also had a leiomyosarcoma of the small intestine.

These results indicated that the combined saturate and aromatic fractions of steam-refined asphalt produced considerably more cancers (32.5%) than the mixed air and steam refined asphalts diluted with benzene (22%) (Simmers et al.,1959) or the pure undiluted steam-refined asphalt (14%) (Simmers,1965a) that the author had tested previously.)

Simmers (1965b) concluded that the combined saturate and aromatic fractions of asphalts have greater cancer producing qualities, as measured by skin application experiments, than pure asphalt. He also noted that while ultraviolet fluorescence is not indicative of oncogenic activity, the results may be related to the presence of carcinogenic PAHs in the fractions which are fluorescent.

Hueper and Payne (1960) investigated the dermal carcinogenic potential of four road (paving grade) asphalts: 3 steam distillation products from Mississippi, California, and Venezuela crudes and 1 steam-vacuum distillation product from an Oklahoma crude. Each asphalt was diluted with a sufficient (unspecified) amount of acetone so that one drop of the material could be applied to the napes of mice, equally distributed by sex. The Venezuelan asphalt was applied twice weekly for a maximal period of 2 years to 100 mice. Each of the other 3 asphalts were similarly applied to 50 mice. Furthermore, each asphalt, undiluted and heated, was painted on the inside of both ears and on a shaved area of the back of 6 rabbits, following the same schedule as that used for the mice. These animals lived in colonies and were administered no control substances. Surviving animals were killed at the end of the 2 year test period. Autopsies were performed on all animals and histologic examinations were made of all tissues which exhibited gross abnormalities.

A summary of the results is presented in Table 4.9. Of the 250 exposed mice, 1 carcinoma and 2 papillomas of the skin were observed and attributed to the asphalts. Seven cases of leukemia also were observed. The authors noted that leukemic reactions occur spontaneously in the train of mice tested, and therefore, they attributed such reactions to the Venezuelan and Oklahoman asphalts. The authors concluded that the tested asphalts possessed mild to moderate carcinogenic properties for the skin and soft tissues of mice and that occupational and environmental exposure may be associated with cancer hazards to the tissues of contact.

Kireeva (1968) studied the carcinogenicity of six different grades of petroleum residues from Russian crude oils. Four of the materials were atmospheric distillation residues possibly suitable as paving-grade asphalts. The other two materials were petroleum cracking residues (petroleum tars) and a discussion of their properties is beyond the scope of this report.

The four atmospheric residues, each in solution with 40% benzene, were painted on mice once a week for 19 months. Control animals were painted with benzene only. The dosages were not reported. Applications were discontinued at the appearance of toxic effects or marked weakening of the animals.

The test results are presented in Table 4.10. For one residue (A) 2 of 50 animals developed skin tumors: 1 squamous-cell and 1 sebaceous-gland adenoma. The first tumor appeared in the 16th month. Pulmonary adenomas and adenocarcinomas were present in 5 mice of this group. In a group of 40 mice exposed to another material (B), no skin tumors developed, but a pulmonary adenoma appeared in one animal. A third residue (C) painted on a group of 50 mice resulted in one subcutaneous fibrosarcoma, one papilloma, one pulmonary adenoma, two lymphoreticular sarcomas and one hepatic hemangioma. The first skin tumor appeared during the 12th month, but regressed during the 13th month. The first persistent skin tumor appeared in the 16th month. One pulmonary adenoma and one skin tumor that regressed were found in 37 mice exposed to a fourth residue (D). The 23 animals in the control group, painted with benzene alone, developed no skin tumors, although one animal developed pulmonary adenomas.

Nontumorogenic effects also were observed in the experimental animals. During the first 4 to 5 months of the experiment, the residue exposed mice lost weight, moved sluggishly, and experienced a marked thinning of the coat. Partial or complete atrophy of the skin papillae and hyperkeratosis with acute and chronic inflammation appeared in many of these animals. Other skin effects included atrophy of the sebaceous glands in the control animals and epidermal atrophy, focal hyperplasia, and atrophy of the hair follicles in both exposed and control groups. Based on a comparison of results among the atmospheric residues and the petroleum tars, the author concluded that a correlation exists between the BaP content of the substances and their carcinogenic activity. No data was presented to support this statement.

Wallcave et al. (1971) attempted to correlate the PAH contents of eight paving grade asphalts with the extent of their tumor induction through skin-painting experiments.

Chemical analyses and separations of the asphalts were carried out by extraction of the parent materials and subsequent chromatography to produce "interference-free" PAH fractions. These fractions were subsequently analyzed for the contents of individual PAH compounds. PAHs were present to some degree in all asphalt samples (Table 2.3). The monomethyl and dimethyl (and/or ethyl) derivatives of most of the PAHs were present in much greater abundance than the unsubstituted PAH compounds. Other derivatives corresponding to trimethyl and tetramethyl substituents also were present. Some heterocyclic PAHs were found in low concentrations in certain asphalts but they are not listed in Table 2.3.

Eight groups of mice, 7 to 11 weeks old with average weights of 20 grams for females and 25 grams for males, were selected for the asphalt painting experiment. A one-inch square zone of hair was shaved from the back of each animal at the beginning of the experiment and was kept free of hair by periodic clipping with scissors. To facilitate application, the asphalts were dissolved in benzene to form 10% solutions. Twenty-five microliters of each material, containing approximately 2.5 mg of asphalt, was applied to the shaved area twice a week. A control group of mice also was painted twice a week with benzene alone. The number of animals in each group that came to autopsy is given in Table 4.11. The mean survival time was 81 weeks for the test animals and 82 weeks for the controls.

The autopsies and histological examinations revealed that the asphalts induced hyperplasia of the epidermis as a general phenomenon, frequently accompanied by inflammatory infiltration of the dermis and on several occasions ulceration with formation of small abscesses. Amyloidosis was frequently observed in the test animals, particularly in the spleen and kidney. Six skin tumors were found in the test animals (2.7%) and one was found in a control (3.8%)(Table 4.11). Subcutaneous and internal tumors were observed in all of the test groups. These include cases of carcinoma of the breast, lung adenoma, malignant lymphoma, papilloma of the stomach, osteoma, pituitary adenoma, endometrial carcinoma, mesothelioma, fibrosarcoma and malignant schwannoma. Tumors were observed eventually in the control group and their character and frequency were not significantly different than in the test groups. The authors noted that the percentage of tumors produced by the asphalts were similar to those reported by Heuper and Payne (1960), but the number of tumors induced was insufficient to permit conclusions with regard to possible connection between PAH content and tumorigenicity.

McKee and Lewis (1987) investigated the dermal carcinogenic potential of raw bitumen derived from the Cold Lake Oil Sands deposit. This deposit has proved to be a viable source of bituminous materials suitable for use in paving applications. The material was recovered from the Clearwater Formation in the deposit through in situ steam injection and further treatment for water removal.

The bitumen was applied in 25 ul aliquots as a 75% suspension in toluene to the interscapular area of 50 male mice, 6 to 10 weeks old, three times weekly for the lifetime of each animal. Negative and vehicle control groups of 50 mice each were treated similarly with highly refined white oil and toluene, respectively. All animals were examined daily for the appearance of dermal tumors. Consideration was limited to squamous cell carcinomas. squamous cell papillomas, and keratoacanthomas which arose at the site of test material application. Upon death, a complete necropsy was performed on each animal. All body cavities were inspected and all grossly diagnosed tumors and some other tissues were examined microscopically.

Repeated application of crude bitumen (approximately 56.25 mg/week) induced skin tumors in 26% of the test animals with a median latency of approximately 2 years (Table 4.12). Neither the negative nor the vehicle control materials induced squamous cell tumors in this study. The bitumen did not significantly influence survival time. A variety of primary tumors of other types also were found during the microscopic examinations (Table 4.13), but in no case did the incidence in the bitumen treatment group significantly exceed that in the negative or vehicle controls. The authors concluded that the Cold Lake bitumen was a moderately active epidermal carcinogen and that the carcinogenic hazards associated with this material were no different from similar materials obtained through conventional petroleum refining operations.

The dermal carcinogenic potentials of bituminous materials and bitumen-derived liquids from the Athabasca Oil Sands deposit have been evaluated by McKee et al. (1986). Discussions of experiments with these materials are beyond the scope of this report.

## Injection Experiments

In conjunction with skin application experiments, several investigations have focused on the carcinogenic potential of injected asphalt. One such study was performed by Simmers et al. (1959). In the experiments, a pooled mixture of steam-refined and air-refined asphalts from six California refineries suspended in olive oil to form a 1% emulsion. A group of 33 male and 29 female mice were injected subcutaneously in the interscapular region with 0.2ml of the suspension twice weekly. After 41 weeks, the frequency of injection was reduced to once a week because of excessive buildup of material in the injected area. A control group of 32 male and 28 female mice were similarly injected with olive oil alone.

Results of the autopsies showed the development of injection site tumors consisting of one rhabdomyosarcoma and seven fibrosarcomas of which the first sarcoma was observed 36 weeks into the study. No evidence of metastasis was reported in any of the tumor bearing animals. In this paper, the authors concluded that pooled asphalt from western U.S. crude sources contains a substance or substances which will cause sarcomas when injected subcutaneously into mice. However, in a subsequent study, Simmers (1965a) suggested that the large volume of injected material in this experiment (Simmers et al., 1959) may have introduced tissue separation as an additional factor in the observed carcinogenesis.

Other experiments by Simmers (1965a) investigated the carcinogenicity of undiluted air-blown and steam-refined asphalts injected into animals. Twenty-five male and 25 female mice were each given one 200 mg subcutaneous injection of steam-refined asphalt in the interscapular region. Composition of the asphalt and its preparation for injection was as previously discussed for skin painting (Simmers, 1965a)(Section 4.2.1). After 111 days, nine male and four females, having no palpable asphalt deposits, were reinjected with another 200 mg/animal of the steam-refined asphalt. A similar group of mice was injected with the same dose of air-blown asphalt. After 120 days, 11 males and 7 females in this second group were reinjected as described above.

The results from this experiment are presented in Table 4.14. Of the mice injected with the steam-refined asphalt, 32 animals came to autopsy and 15 were examined microscopically. One adenoma of the lung was found in this group, but no cancerous growths were reported. Histological examinations revealed that in 5 mice, asphalt was present in locations remote from the site of injection. These sites consisted of the abdominal cavity in one mouse, the thoracic cavity in two, near a kidney in one and in the liver in one mouse. Wherever found, including the injection site, the asphalt was surrounded by a thin, relatively acellular sheath of tissue.

From the air-refined asphalt group, 38 animals came to autopsy resulting in 24 histological examinations. Disclosed were 5 cancerous growths and 5 lung adenomas. One of the cancers was a rhabdomyosarcoma adherent to the muscle of the right thigh and back that had encapsulated the injected asphalt. This growth also metastasized to the animal's left lung and liver. Another rhabdomyosarcoma was found on an animal's abdominal wall that had encapsulated the injected asphalt. A third animal had a tumor at the site of intrascapular injection. This growth apparently arose from skin accessory structures, most probably hair follicle or sebaceous gland, and had almost completely replaced the left lung.

Simmers concluded that the higher incidence of cancer in the air-refined asphalt group may be accounted for by the increase in the complexity of the asphalt molecules that result from the polymerization and condensation mechanisms of the air-blowing process. Simmers also explained that, since the air-blowing process tends to reduce the PAH content in asphalts, and since PAHs may contain "anti-cancer properties" as described by Sampey (1954), the greater presence of PAHs in steam-refined asphalt may lead to greater suppression of cancer production by the carcinogens in this asphalt as compared to air-refined asphalts.

Several additional studies similar to these described have been conducted. The results also indicate that when heavy concentrations of some asphalts or their components are artificially placed in contact with laboratory animals by skin contact or injection, some form of a cancerous growth may result.

## Inhalation Experiments

Studies on the exposure of experimental animals to petroleum asphalt aerosol and smoke were reported by Simmers (1964). In one experiment, 10 male and 10 female mice were exposed to an aerosol of unstated concentration generated from the asphalt mixture described by Simmers (1965b). The aerosol was generated by discharging an emulsion of asphalt in hot water through a nebulizer into a large chamber. The aerosol was admitted in 2-second pulses for 16 seconds in each minute. This periodic pulsation was adequate to maintain a fog of asphalt in water for the full 30 minute daily exposure. Exposures were carried out 5 days a week for up to 82 weeks. The animals were restrained with their muzzles projecting into the aerosol chamber.

Autopsies were performed on 17 mice. Three of these had survived 410 exposures and 10 had survived 280 or more exposures. The number of animals surviving fewer than 280 exposures was not reported.

Another experiment also was conducted to determine the effects of asphalt "smoke" on mice. In this experiment, 21 of the 30 exposed mice were subjected to necropsy. Nine of these mice survived 401 days of exposure to the asphalt smoke and 15 were exposed to the smoke for over 300 days. The last animal was killed after 21.2 months. During the experiment, the inside of the exposure chamber became covered with a yellowish-brown, oily material that had a strong petroleum odor and showed a yellowish-green fluorescence when illuminated with ultraviolet light. The animals whose food was contaminated with this material ate as much and maintained their body weights as well as the animals eating the uncontaminated food. No gross evidence of gastrointestinal tract tumors was found in the animals eating the contaminated food, although a few gross lesions were observed. When examined microscopically these lesions were judged to be neoplastic.

Bronchitis with abscess formation, loss of bronchial cilia, epithelium, along with pneumonitis, were frequent findings in lungs of the animals that had inhaled the asphalt smoke. One bronchial adenoma also was reported. Epithelial hyperplasia occurred occasionally, as did emphysema, often associated with focal lung collapse. Large areas of peribronchial round-cell infiltration were common and extreme bronchial dilatation was sometimes observed, but no tumors were reported.In both experiments, the adverse changes noted in the tracheobronchial tree and lungs of the exposed animals were scattered, with normal areas being found in all animals Some animals were relatively refractory to the smoke and aerosol, while others showed advanced adverse changes after relatively few exposures.

Simmers (1964) stated that the tracheobronchial and pulmonary changes observed in these experiments closely paralleled those described in other experiments on the respiratory effects of various air pollutants. Simmers suggested that the changes in the tracheobronchial trees and lungs of mice breathing air polluted with PAHs might have been nonspecific phenomena and that the degree of change was dose-dependent. Simmers also indicated that these findings paralleled the observed fact that not every human exposed to air pollutants shows the same adverse reactions. From the data presented, no statement proposing a dose-response relationship between PAH content and degree of adverse change can be supported.The adverse effects observed in these animals closely parallel those observed by Hueper and Payne (1960) and indicate again that nonspecific respiratory irritant effects are caused by chronic exposure to high concentrations of asphalt fumes.

In an effort to gain insights to possible cause and effect relationships, researchers at NIOSH (1977) estimated the exposure concentrations for Simmers' (1964) experiment. Indirect calorimetric experiments performed by the NIOSH researchers suggested that airflow through the chamber used by Simmers was probably in the range of 1 to 10 cubic meters per hour (m3/hr). Using these values, the researchers calculated that the exposure concentrations were probably in the range of 74 to 929 milligrams per cubic meter (mg/m3) The NIOSH researchers concluded that the animals in Simmers'(1964) experiment were subjected to considerably higher total exposures than would be expected of humans during a lifetime of work in the asphalt industry.

Mentioned previously, Hueper and Payne (1960) also conducted inhalation experiments on mice. These tests, however, involved the use of roofing-grade asphalts and their review is beyond the scope of this report.

## Other Experiments

Truc and Fleig (1913) reported observations on the effects of asphalt vapor on the eyes of rabbits. The asphalts used for these experiments came from the United States but were not further identified. The asphalt was heated in a retort until a dense oily vapor was generated. The vapor was then directed onto the eyes of immobilized rabbits. Concentrations of vapor in the air contacting the eyes and the durations and frequencies of the exposures were not reported. Only minor transient conjunctivitis was noted in the rabbits exposed to the asphalt vapors. A slight infiltration of the cornea was sometimes noted after frequent exposures, but this disappeared within several days after the exposures ended. No other signs of irritation were observed in the rabbits.

## Summary

This chapter presents reviews of the identifiable reports concerning observed adverse health effects in humans and experimental animals following exposures to paving-grade asphalts and asphalt emissions. The few applicable reports on human health suggested that the noted adverse effects may be associated with exposure to asphalt emissions, but the effects were confounded by many factors. Therefore, this available information provides inadequate evidence that hot-mix asphalt exposures alone adversely affect human health. The animal toxicological studies investigated several routes of controlled exposure. The results provide sufficient evidence that heavy concentrations of artificially applied paving asphalts are slightly carcinogenic, but only to the species and strains of animals used in the experiments. Animal study results cannot be directly extrapolated to potential health effects in humans.

# Chapter 5 Environmental Exposure And Effects

This chapter is intended to discuss exposures to the natural environment and the various impacts that might result from the use of petroleum asphalt in the asphalt paving industry. Very little environmental information has been identified that relates directly to paving asphalts. There is some general information is available regarding environmental exposure to PAHs from other sources and their possible effect. PAHs are present in asphalt (Chapter 2) and asphalt emissions (Chapter 3), and under certain conditions they may have the potential to cause adverse effects in some organisms (Chapters 2 and 4). Although PAHs are a class of compounds that are of primary concern to the environment, recent findings indicate that PAHs do not move easily or far. (Ed.N.unpublished,1991). Therefore, this chapter provides an overview of the potential contribution for environment exposures to paving grade asphalts.

## Exposure to the Environment

Environmental exposure from the use of petroleum asphalt in the paving industry involves the introduction and intercycling of asphalt materials and emissions within the atmospheric, terrestrial and aquatic environments. Exposure theoretically could occur from (Fig.5.1): (a) the processes involved in the construction of asphaltic pavements, and, (b) the wear and degradation of asphaltic pavements caused by human and natural forces. However, little information is known about the character and magnitude of such environmental exposure because documentation on the subject is scarce. Virtually all of the existing data on exposure to asphalt concerns direct occupational exposure of man to bitumen fumes which may be from a number of related products (Chapter 3). In most of these studies, the fumes were physically sampled and their magnitude and character were determined with respect to the amounts and/or distribution of organic and inorganic materials present in the collected samples. Inorganic materials were characterized as mineral particulates and organic substances were characterized as hydrocarbons, specifically PAHs. Information on direct environmental exposure from the use of asphalt in the paving industry is very limited. This section will focus on the known information on created by the paving industry in the use of paving grade asphalts.

## Atmospheric Exposure

All of the reports concerning human exposure to asphalt (Section 4.1) involved the monitoring of atmospheric emissions from the occupational environment. These reports suggest that the character of atmospheric emissions from paving processes may include

PAHs, but the significance of the magnitude of such emissions remains questionable.

U. S. asphalt consumption (Fig. 5.2) has numbered in the tens of millions of tons annually over the last decade. However, estimates of atmospheric PAH emissions (Table 5.1) indicate that exposure from asphalt production, regardless of the type of asphalt,is very small. The other industrialized countries noted support that estimate. The fact that not all of the asphalt produced is used in the asphalt paving industry (Fig. 5.2) supports the estimates that any atmospheric PAH emissions from the use of paving grade asphalts are minimal. Consequently, any deposition of PAHs into the atmosphere from the use of paving grade asphalt cements would also be considered minimal.

## Terrestrial Exposure

Exposure of asphalt emissions, including PAHs, to the land is thought to be by the placement, wear, and degradation of asphalt paving products as well as from asphalt-related PAH emissions that are deposited on land from the atmosphere. No estimates have been found concerning atmospheric deposition, and only one source of information has been identified regarding the magnitude of terrestrial exposure from asphalt pavement surfaces.

Nielson et al. (1969) performed a modest study to evaluate the potential and to determine the amount of asphalt materials which could be washed from road surfaces stabilized with emulsified asphalt. The investigation was sparked by concerns from the U. S. Forest Service that the asphalt materials used in a watershed may wash into the reservoirs that serve Portland, Oregon, thereby creating a possible water quality problem. The study emphasized the leaching potential from emulsified asphalts, which are beyond the scope of this review, but the study also compared the results to the measured leachings from a hot-mix asphalt pavement.

This study was extremely artificial and no usable data that is applicable to potential hot-mix asphalt pavement leaching was generated. The description of the experiment is presented here for informational purposes relative to other asphalt usages.

A simulated hot-mix pavement was formed by mixing dry sand and hot asphalt cement in proportions of 3.9 g of sand to 1 g asphalt and placing the material on 12 inch square steel plates at a thickness of approximately 0.125 inch, leaving a one inch margin on each edge of the plate. The temperature of placement was 140° C (284° F). All of the plates were cured in the laboratory at 21° C (70° F) for various lengths of time. Periodically, two plates were placed in 12 inch square funnels. Simulated rainfall, approaching normal rainfall conditions for the region, was applied by use of a fine-sprinkler hose at an average rate of 1.5 in/hr. The runoff from one hour of simulation was processed as described in the article to obtain an asphalt residue. The data collected (Table 5.2) and a plot of the results (Fig. 5.3) are presented.

The study showed that considerable asphalt could be washed from the simulated pavement during the first few days after application. The authors calculated this value to be equivalent to 0.8 lb per mile of pavement, assuming a 20 foot road width. After a few days of curing, the amount removable declined rapidly to approximately 2 percent of the amount applied and remained practically constant for the 12-day duration of the simulation. The authors emphasized that this laboratory study was conducted under extreme conditions and that the results should be considered accordingly when comparing them to actual circumstances in field practice. Three significant factors should be addressed more specifically. (1) The mixture of sand and asphalt is not a simulation of a well designed hot-mix asphalt pavement (HMAC). HMAC is a combination of specifically sized aggregates designed to combine in such a way to provide the stability required when combined with the proper amount of asphalt and properly compacted to maintain that stability and seal the mixture from the incursion of moisture. (2) The simulated hot-mix surface was not compacted and prepared with five to six times the quantity of asphalt cement than is commonly used in hot-mix asphalt concrete. Such an excess will slow the curing rate for the pavement, increase the amount of asphalt cement exposed and permit the artificial rainfall to penetrate the thinly placed mixture, thereby increasing the potential leachability. (3) Newly placed hot-mix asphalt pavements are compacted to a density that will retard the penetration of moisture, thus reducing potential leachability.

The Asphalt Institute (1989a) has reported that the estimated total length of all types of asphalt pavements in the contiguous United States is about 2,030,000 miles (Fig. 5.4). Some of this material is likely to be removed by rainfall, but estimates of the magnitude and character of such leachable substances must be made with great caution. The only identifiable leaching study is very crude and exaggerates the potential emissions.

## Aquatic Exposure

Any potential exposure of the aquatic environment to asphalt paving emissions would occur indirectly through surface runoff from land and fallout and rainout from the atmosphere. Again, there are no identifiable reports that estimate the character or magnitude of any such exposure from asphalt pavements. Groundwater and reservoir water generally contain PAH concentrations which are lower than those in river water by a factor of ten or more. Rainwater may contain concentrations of PAHs as high as those in some rivers (Von Hellmann, 1974) and represents another route to land and water contamination from airborne PAHs. Concentrations of PAHs in stormwater runoff have been seen to increase markedly during heavy rainfall as a result of airborne rainout as well as runoff from road surfaces and may include some leaching of various asphalt type pavements (Osborne and Crosby, 1987), but no supporting data were provided to differentiate between the contributions from each of the sources.

## Summary

Very little data is available concerning environmental exposure to PAH emissions from the asphalt paving industry. Rough estimates suggest that the total exposure is very low. The lack of identifiable reports on studies concerning the impact of any environmental exposure to both the earth and water plus the apparent minimal effect on the atmosphere are indications that the total exposure is, in fact, very low.

# Chapter 6 Aspects Of Human Safety

There has been and continues to be a strong emphasis on personal safety in the workplace when handling asphalt cement and asphalt concrete mixtures (1,2,3,4)*. A number of national and state agencies have been created for the sole purpose of developing, maintaining, and enforcing guidelines for this purpose. This chapter will not attempt to duplicate those guidelines unnecessarily, but, instead, will refer to them where appropriate.

The safety and health considerations within a refinery operation are highly specialized and are closely controlled (5). This discussion will thus be limited to the handling and use of the asphalt cement after it leaves the refinery, with the understanding that the safety considerations applicable to asphalt cement at the asphalt concrete mix production plant and during placement and compaction of the mix on the roadway also apply to the handling of the material during the asphalt operation portion at the refinery.

There is a fine line that divides a safety consideration or hazard from a health problem. The issues of fume inhalation and other types of exposure are discussed elsewhere in this report and will not be repeated here.

* (-) refers to numbered safety references at end of report

## Objective

The objective of this chapter is to develop a summary of available information from all identifiable existing sources on the potential problems regarding the safe handling and use of asphalt cement and asphalt concrete mixtures in the asphalt paving industry. Emphasis is placed on two primary areas of concern: (a) burns from handling hot asphalt cement and asphalt concrete mixtures, and (b) dangers from fires and explosions in regard to the use of these materials.

It was originally speculated that two additional areas of possible concern might be included in the Safety area of concern. These two areas were asphalt fumes and heat stress. It was decided, however, that the asphalt fume issue would better be discussed within the health sections of this report. In regard to the subject of heat stress, there is essentially no data in the literature that deals with asphalt paving operations-- either the production of the mix at the batch or drum plant or at the roadway laydown site. Thus heat stress was eliminated from consideration for inclusion in this chapter.

## Reference Organizations

Fourteen different organizations and agencies were contacted to gain information on the safety aspects of handling asphalt and asphalt concrete mixtures. Those organizations were as follows:

1. American Conference of Governmental Industrial Hygienists
2. American National Standards Institute
3. American Petroleum Institute
4. The Asphalt Institute
5. Asphalt Roofing Manufacturers Association
6. Associated General Contractors of America
7. International Occupational Safety and Health Information Center
8. Marion Laboratories Library
9. National Asphalt Pavement Association
10. National Institute for Occupational Safety and Health
11. National Roofing Contractors Association
12. National Safety Council
13. Occupational Safety and Health Administration
14. Transportation Research Board Information Search

## Burns

Asphalt cement is hot. An asphalt concrete mixture is hot. Because of their elevated temperature that exists even past the completion of the total paving operation, there is always a danger of burns when handling both the asphalt cement and the asphalt concrete mixture. Depending upon its grade (by either the penetration or viscosity grading system), asphalt is typically delivered to an asphalt plant at a temperature of 275 F to 450 F, but usually in the range of 300 F to 330 F. When mixed with aggregate to produce an asphalt concrete mixture, the normal temperature of the resulting mixture is typically in the range of 270 F to 310 F, with extremes of mix temperature occurring from a low of approximately 240 F to a high of 380 F when some particular additives are added to the asphalt cement during or prior to the mixing with aggregate.

Because of the high temperatures involved with the handling of the asphalt cements, certain precautions must be taken to prevent burns from occurring (6). The amount of skin exposed should be kept to a minimum by wearing appropriate clothing, footwear, and gloves. A face shield, goggles or safety glasses should be used to protect the eyes and face from accidental contact with the hot asphalt and potential burns. As discussed in greater detail later in this chapter, special procedures are required to remove asphalt cement from the skin without inflicting additional damage to the skin. This removal should be done only under medical supervision.

## Transportation Of Asphalt Cement

Asphalt cement can be transported from the refinery where it is produced to the asphalt concrete production plant in one of three primary ways. The most common method of transportation is by tank truck. The other two methods sometimes used are railroad tank car and barge. In some cases, a combination of these modes of transport are used--the first part of the journey by rail car with final delivery to the plant by tank truck, for example. The safety aspects of handling asphalt cements are essentially the same regardless of the means used to transport the material (7). In the following discussion, the term "tank" is used to indicate either tank truck, railroad tank car or waterways barge.

The first essential safety concern is that the tank used to hold the hot asphalt cement is clean. Table 6.1 indicates that it is permissible to load asphalt cements into a tank that has had asphalt cement as the last product in that tank (8). If a cutback asphalt, asphalt emulsion or residual fuel oil had been the material previously hauled or stored, The tank should be empty with no measurable quantity of material left in the bottom of the tank. If any other product had previously been in the tank, that tank must be completely cleaned before the asphalt cement is delivered to that storage tank or transport vessel.

If water is left in the bottom of the tank truck, railroad car or barge, there is a potential problem of frothing or boilover (9). Depending on the amount of material remaining in the tank before the hot asphalt is introduced, it is possible for the heat from the asphalt cement to cause any free water in the bottom of the tank or the water in an asphalt emulsion to boil or foam. This can cause severe bubbling and frothing of the asphalt cement and may allow the material to rapidly spill over the top of the tank, causing burn injuries to personnel involved in the asphalt cement loading operation (10).

Potential problems with foaming or frothing can be reduced by assuring that the tank is empty before loading commences and by keeping all hatches, except the one being used to load the asphalt cement, closed during the loading operation. In addition, if the tank is equipped with steam coils or heaters to keep the asphalt cement hot during transport or storage, those coils or heaters need to be free of leaks. Cycling of the temperature of the asphalt cement material in the tank should be avoided to prevent moisture from condensing and accumulating in the tank. The temperatures should be as low as practical and still maintain the fluidity and pumpability of the asphalt cement. Furthermore, the temperature should be carefully controlled so that large fluctuations do not occur.

Another potential problem during the loading and transport of the asphalt cement is vapor flashing (9,10). The presence of hydrocarbon vapors plus air and an ignition source can result in a fire or an explosion. To reduce the possibility of vapor flashing, the temperature of the asphalt cement should be as low as possible. All sources of ignition should be eliminated at all times. In addition, air should not be used to blow out the tank prior to loading the asphalt cement. This subject is discussed in more detailed in the section on Fire and Explosion.

Another safety hazard to be cognizant of in the handling of hot asphalt cement is concerned with the generation of hydrogen sulfide which is a product of the reaction between hydrogen and sulfur present in the asphalt cement (1,15,16). Low concentrations of hydrogen sulfide are detected by a rotten egg odor. High concentrations of hydrogen sulfide, however, are not easily detectable because the odor is masked by other hydrocarbon emissions. Hydrogen sulfide can quickly render a person unconscious and may cause death if fresh air is deprived and breathing stops. Thus extreme caution must be used when loading or unloading asphalt cement to prevent the inhalation of the concentrated fumes from the tank.

Care should be exercised to assure that the tank used to transport the hot asphalt cement is structurally sound. Failure of the tank truck, the railroad tank car, or the barge can occur from a variety of causes including corrosion, the accumulation of asphalt cement on the underside of the roof of the tank, and excessive pressure in the tank. All tanks should be cleaned and then inspected on a regular basis.

## Storage Of Asphalt Cement At The Asphalt Concrete Plant

Once the asphalt cement has arrived at the asphalt concrete production plant, it must be offloaded from the transport vehicle. The storage tank used is typically a cylindrical shell that is placed in either a vertical or horizontal position. The roof of the tank contains vents and hatches, including manway covers. Most tanks are insulated and all are heated, either with steam, hot oil coils, hot air heaters, or electric heaters.

The same guidelines that are used for the transport tank are applicable to the storage tank at the plant site. It is permissible to load asphalt cement into a tank that has previously held asphalt cement, regardless of grade. If any other asphalt products, such as cutback asphalt or asphalt emulsion, or any type of residual fuel oil has been stored in the tank, the tank must be completely empty before the new asphalt cement is pumped into the tank. Tanks used to store any other products must be cleaned before the asphalt cement is offloaded into the tank. In addition, potential problems with foaming and frothing, vapor flashing, and tank failure are similar for the plant tanks as for the tanks used to transport the asphalt cement.

Because asphalt cement is hot (typically between 300 F and 350 F), the possibility of burns is significant when the actual material is touched or when the tanks and lines used to store and move the material come into contact with exposed skin. The pipes and lines used to transport the asphalt cement to the asphalt batch or drum mix plant from the storage tank should be insulated. This reduces the possibility of burns. Properly handled, there should be no reason for a person come in contact with the asphalt cement, itself, but contact with the equipment used to handle the material can also cause severe burns.

## Laboratory Testing

At the asphalt concrete plant site or at a separate facility, testing is done using both asphalt cement and asphalt concrete mixtures. This test work involves determining the properties of the asphalt binder material, mixing the asphalt cement with the aggregates to produce an asphalt concrete mix, and determining the properties of the mixture. These procedures all involve handling hot materials, both the asphalt cement and the asphalt concrete mixture. Burns are possible whenever these materials are being used, handled and/or tested. The same precautions need to be exercised in the laboratory that are required at the mixing plant. Productive clothing and footwear should be worn and an eye/face shield should be used.

## Production Of The Asphalt Concrete Mixture

The asphalt cement is pumped from the storage tank to the mixing plant. There the material is discharged from a pipe and weigh bucket into the pugmill of the batch plant or through the rear of dryer drum into the coating section of the drum mix plant. During this delivery and mixing process, the asphalt cement is isolated form contact with plant personnel and burns should not be a problem. In addition, the asphalt cement ceases to be a separate material at this point in the process where it becomes incorporated into the asphalt concrete mixture.

When mixing of the asphalt cement and the aggregate is completed, the asphalt concrete material is discharged from the plant. Sometimes, from the batch plant, it is deposited directly into the haul truck for delivery to the paving site. In a drum mix plant and some batch plant processes, the mixture, which is typically at a temperature of 270 F to 310 F, is placed first in a temporary storage silo and then discharged into a haul truck for delivery to the paver. Because of the temperature of the asphalt concrete mix, the potential for burns is significant if the material comes in contact with exposed skin. Except for the mix sampling for the purpose of performing laboratory testing, however, there is not any reason why an individual should come in contact with the mix during the mixing and loading operations.

## Transportation And Placement Of The Asphalt Concrete Mixture

The manufactured asphalt concrete mix is discharged into the haul truck to transport to the paving site. Burns are possible whenever the mix may come in contact with exposed skin of any of the personnel involved in the placement process. Contact may occur when the driver of the truck covers or uncovers the load with a tarpaulin, when a sample of the loose mixture is taken from the body of the truck, the paver hopper or from the uncompacted mat immediately behind the paver. Other locations to exercise extra precaution are when the workers clean off the tailgate of the haul truck, feeding the mixture into the paver from the wings of the paver hopper and when the rakers are manually manipulating the loose material during the construction of a longitudinal joint or any other required hand work. Although the mix is cooling and the temperature is reduced the placement operation, the mixture is still normally above 240 F at the time it comes out from beneath the paver screed.

Burns are possible during the placement operation if any of the contractor or inspection agency personnel walk or stand on the hot mix material. If proper footwear is worn, burns to the soles of the feet are not typically a problem (11). In addition, the individuals around the paver usually do not stand on the mix for any significant amount of time. Thus most of he burn injuries that occur at the laydown or placement site are related to the hot mix material coming in contact with exposed skin.

The compaction operation normally does not pose a significant potential for burns. The roller operators are on top of the rollers and away from direct exposure to the hot mix. Further, the mix is cooling through the compaction process and usually has a temperature in the range of 150 F to 250 F. Burns are certainly possible, however, if any of the paving personnel become careless and touch the hot mix during the placement or compaction operations.

## First Aid For Burns

The National Asphalt Pavement Association has published information on the procedures for suggested treatment for molten asphalt cement burns (12). That information states that the affected burn area should be completely submerged in ice water. It also states that the burned area can be submerged in cold tap water. A further suggestion is that the affected area be placed under running water. It is stated that ice should not be applied directly to the burned area.

This same information indicates that no attempt should be made to remove the asphalt cement from the burned area because of the almost certain removal of viable skin and hair follicles under the asphalt cement. In addition, products containing solvents or ammonia should never be applied. Normally, separation of the asphalt cement from the skin will occur naturally in 48 to 72 hours. It is further suggested that, if early removal of the asphalt cement is necessary, a bandage should be soaked in mineral oil and placed over the asphalt cement for 2 to 3 hours to soften the asphalt cement before removal of the material is attempted.

For minor asphalt cement burns, the individual burned should be treated by a physician as quickly as possible. For serious burns, the injury should be treated at a hospital as soon as possible. Further, the individual should be treated for shock. The person should be kept lying down and quiet with his head lower than his feet and should be covered with a blanket to keep the body temperature normal.

The advice to completely submerge the affected area in ice water is the subject of some difference of opinion. It has been suggested that cold water rather than ice be used to reduce the chance of hypothermia (13,14,15). In addition, it is pointed out that fluids resuscitation is required for people who have been burned over a large part of their bodies.

Most references to burns with bituminous materials are based on those caused by tar and roofing asphalt cement. Despite the differences in the chemical makeup of these two materials compared to paving asphalt, the resulting characteristics of asphalt cement and tar burns are essentially the same (16,17). A paper entitled "Management of Tar and Asphalt

Injuries" provides some information on materials that can be used to remove tar and asphalt cement from the skin (18). It was pointed out that numerous solvents have been used in the past but that the results were quite variable. Materials tried included mineral oil, kerosene, gasoline, alcohol, acetone, ether, and aldehydes. It was stated, however, that all of these materials "are relatively ineffective and can induce further tissue damage and occasionally produce systemic toxicity through absorption" (X). Among the products that were recommended to remove the asphalt cement were petrolatum, De-Solv-it, Neosporin, Polysorbate, and Tween 80.

One of the primary problems with burns is the risk of infection if the burn is not treated quickly and properly. Thus removal of the asphalt cement should take place relatively soon, by qualified medical personnel, using one of the recommended materials. Once the asphalt cement has been removed, the burn is treated as any other burn.

## Protective Clothing

To prevent most burns from occurring, protective clothing should be worn when handling hot asphalt cement and hot asphalt concrete mixtures (4,19,20,21,22). Loose clothing in good condition should be worn. The collar and the sleeves should be buttoned. Gloves, with gauntlets that extend above the sleeves of the shirt at the wrist, should be worn loosely so that they can be quickly and easily removed if hot asphalt cement is spilled on them. Boots should be worn that have tops at least six inches high. Pants, without cuffs, should extend down over the tops of the boots. A face shield or goggles should be worn to protect the face and eyes.

## Fire And Explosion

An additional safety hazard in regard to the use of asphalt cement is the potential for fire and explosion (5,19,23,24,25). This is a problem because asphalt cement will support combustion under the proper conditions. When mixed with aggregate to make an asphalt concrete mixture, however, the asphalt cement is such a small portion of the total volume and weight of the completed mixture ( typically between 4 and 6 percent) that the mixture itself will not burn at the temperatures involved.

Two threshold temperatures for asphalt cement are the flash point and fire point of the material (26). Flash point is defined as the lowest temperature, corrected to a barometric pressure of 760 mm hg, at which application of a test flame causes the vapor of a test specimen to ignite under the specified conditions of the test (27). Fire point is defined as the lowest temperature at which a specimen will sustain burning for 5 seconds (27).

For asphalt cement, the Cleveland Open Cup method (ASTM Designation D 92) is used to measure both the flash point and the fire point of the material(27). In this procedure, as stated in Section 4, Summary of method, "The test cup is filled to a specified level with the sample. The temperature of the sample is increased rapidly at first and at a slower constant rate as the flash point is approached. At specified intervals a small test flame is passed across the cup. The lowest temperature at which application of the test flame causes the vapors above the surface of the liquid to ignite is taken as the flash point. To determine the fire point, the test is continued until the temperature reaches the point at which the application of the test flame causes the oil to ignite and burn for at least 5 seconds."

For asphalt cements, the average flash point temperatures are given in the following table (27).

The actual flash point temperature is a function of both the type and grade of the asphalt cement. Three different primary classifications are provided: penetration graded asphalt cement, original viscosity graded asphalt cement and for aged residue graded asphalt cement.

| Type and Grade of Asphalt Cement | Reference Specification | Minimum Flash Temperature (F) |
|---|---|---|
| Penetration Graded | ASTM D 946 | |
| 40-50 | | 450 |
| 60-70 | | 450 |
| 85-100 | | 450 |
| 120-150 | | 425 |
| 200-300 | | 350 |
| Viscosity Graded | ASTM D 3381 | |
| 2.5 | | 325 |
| 5 | | 350 |
| 10 | | 425 |
| 20 | | 450 |
| 40 | | 450 |
| Aged Residue Graded | ASTM D 3381 | |
| 1000 | | 400 |
| 2000 | | 425 |
| 4000 | | 440 |
| 8000 | | 450 |
| 16000 | | 460 |

In the vast majority of the cases, except when certain additives are added to very soft ( high penetration or low viscosity) asphalts cements, the binder material is used at a temperature which is below the minimum flash point of the material. Thus the danger of fire or explosion is typically minimal when handling asphalt cement. As previously stated, there is virtually no danger of either fire or explosion once the asphalt is added to the aggregate in the asphalt mixing batch or drum mix plant to produce the asphalt concrete mixture.

## Fire Triangle

For combustion to occur, three different elements must be present. The first is fuel. Asphalt cement can be considered to be a fuel at an appropriate high temperature since it will burn under the proper conditions. The second element is oxygen. Enough oxygen must be available for burning to occur. The third element in the triangle is a source of ignition, a spark, flame or an incandescent material such as a cigarette. The fire triangle requires that all three elements be present for fire to occur (8,28). If any one of the three sides of the triangle is missing, combustion will not occur.

Asphalt cement has been shown to be able to support combustion if the temperature is high enough and if enough oxygen is present. That temperature must be above the flash point of the particular type and grade of asphalt cement being used. The temperature must also be above the fire point for the material, although the fire point is not normally measured for asphalt cement and ASTM specifications do not list minimum values for fire point for the different grades of the materials.

## Transportation Of Asphalt Cement

As previously discussed, asphalt cement is transported from the refinery to the asphalt concrete production plant by tank truck, railroad tank car or barge. When the material is derived from crude oil at the refinery, it is manufactured at an elevated temperature, a temperature that is well above the minimum flash point of the material. When the asphalt cement enters the storage tank at the refinery, its temperature can be over 500 F. If the material is allowed to stay in the storage tank for a period of time, the temperature will be reduced to that of the asphalt cement already in the tank, which is usually in the range of 325 to 375 F.

If the temperature of the asphalt cement has stabilized at normal storage temperatures, the material will be below the minimum flash point temperature for most asphalt cements except for the very softest grades (200-300 penetration grade and AC-2.5 and AC-5 viscosity grade). Further, since the ASTM standards are minimum flash point temperatures, the actual flash point of the asphalt cement may be well above the minimum value given in the specifications.

At times when asphalt cement demand is great, such as in the middle of the summer paving season, or when the refinery has been shut down temporarily for maintenance, the supply of asphalt cement may be low. Then the material may be pumped from the refining tower to the storage tank at a temperature well above its flash point and not remain in the storage tank long enough for its temperature to be reduced significantly. It is possible, therefore, that the asphalt cement could be loaded into the transport vehicle at a temperature over 460 F. In this situation, the temperature of the asphalt cement would be above the minimum flash point. Fire could be a potential problem if enough oxygen were available and if a source of ignition was present.

Asphalt cement is refined by a number of different methods and refining processes. In some cases, some light hydrocarbons or highly volatile material may remain in the asphalt cement. If this occurs, the presence of vapors in the asphalt cement at elevated temperatures could increase and thus lower the flash point of the asphalt cement to some degree. This would, in turn, increase the potential for fire.

It is doubtful if asphalt cement would ever explode. The only way that an explosion could take place in an asphalt cement tank is if there was a great amount of volatile vapors present in the tank when the asphalt cement was loaded and if a source of ignition was present, along with a large supply of oxygen. Explosions of asphalt cement tanks are a very rare occurrence.

## Storage Of Asphalt Cement At The Asphalt Concrete Plant

The chance of a fire in the asphalt cement storage tank at the asphalt concrete batch or drum mix plant is remote because the temperature of the binder material (typically between 300 and 350 F) is normally well below the flash point of the asphalt cement. The pertinent points discussed previously in regard to the loading of asphalt cement into the haul vehicle at the refinery are also applicable to the unloading of the material from the transporting vehicle at the asphalt concrete production plant. The accumulation of light hydrocarbon materials on the underside of the top of the storage tank may be sufficient to allow combustion of the asphalt cement even though its temperature is below its normal flash point.

The information concerning the fire triangle is valid,i.e., the need for an ample supply of oxygen and a source of ignition. To prevent a fire from occurring, it is very important that any open flames or sparks be kept away from the asphalt cement storage tank.

The Asphalt Institute provides a set of guidelines to help prevent fires in asphalt cement storage tanks. This information is as follows (8):

1. Clean roof vents periodically to prevent accumulation of asphalt deposits from vapor accumulation.
2. Use mushroom or cone shaped vents to minimize deposit build up and vent plugging.
3. Prevent insulation near roof vents from becoming saturated with deposits caused by escaping asphalt fumes. Keep filters clean.
4. Provide only one vent for each tank.
5. Keep gauge hatches and manway covers closed.
6. Do not blow out asphalt lines with air and do not blow air into asphalt tanks when the asphalt temperature is above 400 F.
7. Blanket the tank vapor space with an inert gas. An oxygen content of about five percent will help prevent the formation of pyrophoric iron sulfide.

If a fire does occur, water or foam should be applied to the burning asphalt cement with care so that the force of the water does not cause the burning material to spread. Further, the addition of water to the hot asphalt cement may cause severe foaming and frothing of the material and further spread the fire. Finally, the possibility of explosion may increase as volatile hydrocarbon materials are driven off from the asphalt cement because of the heat from the fire.

## Laboratory Testing

The danger of fire and/or explosion at a testing laboratory can be significant because of the amount of volatile material often present in the laboratory. If light hydrocarbon materials remain in the asphalt cement at the end of the refining process and if the asphalt cement is overheated in he laboratory, the presence of volatile vapors in the binder material will increase. The ovens used in some laboratories are multipurpose devices and as such are used to heat a variety of materials including aggregate and polymer modified materials. In addition, uniform control of the temperature in the oven may not be possible due to poor maintenance or malfunctioning equipment. This may allow the temperature of the asphalt cement in the laboratory oven to approach or even exceed the flash point. This possibility would increase the potential for fire if a source of ignition was present since more than an adequate supply of oxygen would normally be available.

The greatest potential problem is the fact that the typical testing laboratory contains many materials which are flammable. A fire which starts in these materials may spread to the asphalt cement. Because the supply of asphalt cement at the laboratory is normally quite small, however, it is doubtful that the asphalt cement itself would add any significant amount of fuel to a fire.

## Production, Transportation, And Placement Of The Asphalt Concrete Mixture

Because the asphalt cement is mixed with the aggregate in the asphalt concrete production plant and because the aggregate will not support combustion, there is no danger of a fire or explosion after the mix has produced in the batch or drum mix plant. Therefore,the transportation of the mix from the plant and the subsequent placement and compaction of the asphalt concrete mixture by the paver and the rollers does not present any potential fire or explosion problems.

# Chapter 7 Summary And Conclusions

This document presents a review of existing information concerning the health and safety of man and the environment as related to the use of petroleum asphalt in the asphalt paving industry. The information in this chapter includes the following: (1) a summary of the information and conclusions presented in this review, (2) identification of the health aspects of primary concern, and (3) suggested areas of needed attention and research.

## Summary of Information

This literature survey is the result of a specific study conducted under of the Strategic Highway Research Program A-001 contract. The purpose of this survey was to establish a current and complete summary of existing knowledge regarding the health and safety aspects of petroleum asphalts used in the asphalt paving industry. No new research was intended for this task. Rather, a state-of-the-art report was to be developed based on a review of the identifiable and pertinent literature.

## Asphalt

Asphalt as defined in the SHRP asphalt research program is a petroleum-derived material used widely by man for its thermoplastic and cementitious characteristics. It is a complex mixture of organic compounds whose molecules are composed predominantly of cyclic hydrocarbons and a lesser quantity of saturated hydrocarbons, as well as heteromolecules containing sulfur, oxygen, nitrogen, and trace amounts of metals. The chemical characterization of asphalt is based on its separation into generic classes of compounds that are complex mixtures; not well-defined chemical species. Asphalt's physical behavior can be explained by considering it to be a colloidal system whose properties are influenced by the concentrations and distribution of the generic compound fractions.

An individual asphalt's overall composition depends on the composition of the crude petroleum from which it is derived as well as the techniques used to refine and process it. Asphalt is obtained primarily through atmospheric, vacuum, and steam distillation processes. These techniques remove lower molecular weight hydrocarbons from the crude oil, leaving the heavier components as a residue. Asphalt is often processed further through solvent precipitation, which removes some saturated compounds while leaving aromatic ring structures, or through air-blowing, which transforms some saturates into cyclics and some cyclics into asphaltenes. To accommodate particular end-use applications, the various processed residues are then blended to obtain an asphaltic product with the desired physical characteristics.

## Human Exposure to Asphalt Emissions

Relatively little information has been identified regarding the direct exposure of man to emissions generated through the use of petroleum asphalt in the hot-mix paving industry. Direct exposure to man was defined in this review as the occupational exposure that workers may experience while performing the various duties required in the industry. The identifiable investigations pertinent to this topic essentially attempted to: (a) identify the physical character of asphalt fumes, (b) estimate atmospheric concentrations and respiratory exposures to these fumes, and (c) relate any possible observed biological responses in workers to a measure of the exposure to mutagenic and/or carcinogenic agents in the fumes.

Standards of exposure limits for asphalt fumes have been established in several nations. However, these standards are vague because they treat asphalt fumes as a specific entity or substance regardless of origin. On the contrary, the term "asphalt fumes" is generic since the emissions are complex mixtures of organic and inorganic materials. Organic matter, composed of various hydrocarbons, exists in the fumes as a gas, as well as adsorbed to the inorganic matter, which are mineral particulates. Hence, a given emission of asphalt fumes can include a variety of other similar matter and can be measured at various concentrations depending on the sampling and analytical techniques employed in the monitoring effort.

The studies on emissions sampling provide only a few approximations of the character and magnitude of asphalt fumes and direct respiratory exposures to workers and tell very little about the effect of direct exposure to the skin of man. Some of these studies also included factors that may confound any assessments of "typical" exposures from the various industry processes. These factors include: (1) inconsistencies in sampling and analysis procedures among investigators, and (2) the concurrent sampling of extraneous matter (e.g., engine exhausts or tobacco smoke) from external sources. Therefore, the available physical sampling data do not provide a detailed description of the occupational exposures in the asphalt paving industry. Nonetheless, the limited data do suggest several important points:

(1) Occupational exposures to workers commonly fell below 5 $mg/m^3$.
(2) Particulate matter usually comprised the predominant material sampled in personal respiratory monitoring.
(3) The predominant sizes of particulates sampled during the monitoring of industry processes were within the respirable range (i.e., less than 10$\mu$m).
(4) The organic fraction (material soluble in low molecular weight hydrocarbons) of sampled particulate matter varied widely (less than 10% to greater than 50%) among duties involved in the paving industry.
(5) Processes involving physical disturbance of the asphalt materials (e.g., tank truck loading or feeding hot-mix through the paver) typically produced greater emissions than other processes (e.g., hot-mix compaction).

## Effects on Human Health

Clinical and epidemiological reports provide accounts of adverse health effects in man potentially associated with occupational and/or environmental exposure to asphalt materials and their emissions. The reported toxic effects from short-term exposures included headaches, nausea, and general irritation of the skin, eyes, and respiratory system. Data on any adverse effects possibly incurred from long-term exposures to paving grade asphalt cements was very limited but appeared to indicate minimal effects. The identifiable reports were few in number and covered a wide range in their applicability to this review. The reports did suggest that adverse effects may be partially attributable to exposure to asphalt emissions, but there were many factors that confounded the available information. These factors included the following: (a) previous and/or concomitant occupational exposures to substances other than asphalt (e.g., coal-derived products, petroleum solvents, insecticides, etc.), (b) exposure magnitudes that were potentially not representative of those in the hot-mix paving industry, (c) non-occupational risk factors, (e.g., tobacco smoking, alcohol consumption, dietary habits, recreational activities, etc.), and (d) the healthy worker effect that is commonly associated with strenuous occupations. Therefore, the available information did not provide evidence that asphalt cement or hot-mix asphalt concrete exposures alone adversely affect human health.

The lack of adequate information concerning effects on humans was supplemented by animal toxicological studies. These studies involved the testing of laboratory mammals to determine the potential mutagenicity and/or carcinogenicity effect of asphalt by various methods of controlled exposure. Such exposure included dermal applications and subcutaneous and intramuscular injections of asphalt cement as well as inhalation of asphalt aerosol and smoke.

The identifiable toxicological studies provided evidence of the slight mutagenicity and carcinogenicity of paving-grade asphalts to experimental animals under extreme and exaggerated conditions of exposure.

## Environmental Exposure to Asphalt Emissions

Very little information is available regarding environmental exposure to asphalt emissions. Results from direct human exposure monitoring indicate that the physical character of asphalt emissions released to the atmosphere during paving operations is composed of mineral particulate matter and hydrocarbons, including higher molecular weight PAHs. Estimates of total atmospheric PAH emissions suggest that the contributions from the paving industry are very small in the America. The PAHs that are released will primarily adsorb to airborne particulate matter. Some of these PAHs will be deposited in a few days, while some may remain in the atmosphere for several weeks.

No information is available concerning the deposition of airborne asphalt emissions onto land.

Finally, there is no identifiable information on aquatic exposure to asphalt emissions or terrestrial exposure from the leaching of pavements with the use of paving grade asphalt cements. However, it can be estimated that the magnitude of such exposure is small.

## Safety Aspects

Primary areas of concern in the handling and await of paving grade asphalt cements are burns, fires and explosions. The high temperatures common in the production of hot mix asphalt concrete and its placement in the road way can cause severe burns if contact with the skin occurs. The transmission lines and handling equipment are also at elevated temperatures and will cause burns when contacted.

Although the temperatures of the asphalt are elevated enough to cause severe burns if there is skin contact, they are generally below the flash point or ignition point. Under some conditions, however, particularly during a rush season or shortage of asphalt, the temperature of the asphalt being transferred from the refinery storage to the transporting vehicle may be borderline or above those values. Caution should always be adhered to in all phases of the use of asphalt cements.

Placing hot asphalt cement into a tank, either storage or transporting vessel, that has held any material other than an asphalt cement can cause a dangerous condition to exist or occur. Foaming and/or boilover can occur if residual material in the tank was water or emulsified asphalt which may endanger the handlers.

In addition, care must be taken to avoid exposure to potential concentrations of hydrogen sulfide fumes. Although normally only unpleasant odors exist in open areas where concentration is light, heavy concentrations such as might exist in a tank are not as easily detected and can cause loss of consciousness and even death.

## Conclusions

Based on the identifiable literature, the following is a list of the primary conclusions can be drawn regarding aspects of the health and safety of man and the environment associated with the use of petroleum based asphalt cement in the hot mix paving industry:

- Paving-grade asphalt cements contain PAHs; a class of organic compounds in which only a small fraction possess mutagenic and carcinogenic properties.
- Asphalt cements contain PAHs in quantities that are several orders of magnitude less than the quantities in coal-tar pitches.
- Emissions from the use of asphalt cements in the paving industry consist mainly of asphalt fumes.
- Caution should be used in exposure to asphalt fumes containing hydrogen sulfide.
- Any PAHs in asphalt emissions from the paving industry consist mainly of higher molecular weight compounds ranging from 3 to 6 rings.

- Industry processes that physically handle the asphalt cements by pumping, mixing, etc. typically generate greater emissions of asphalt fumes than other processes.
- The limited data from emissions sampling studies suggest that occupational exposures to asphalt fumes commonly fall below 5 $mg/m^3$.
- Samples of asphalt fumes are often contaminated by emissions, including PAHs, from other sources (e.g., tobacco smoke or engine exhaust).
- The procedure and equipment used for the sampling and analysis of asphalt emissions were not consistent among investigators involved in the assessment of exposure to paving asphalts.
- Tobacco smoking is a major confounding factor in human biological reactions to asphalt fumes. These results also suggest strong synergistic reactions when asphalt fume exposure is combined with smoking.
- Animal studies indicate potential adverse human health effects when the specimens were subjected to exaggerated dosages.
- The use of petroleum based asphalt in the paving industry contributes less than 1% to the total burden of PAH in the environment.
- Care should be utilized in the handling of liquid asphalt and the hot asphalt-aggregate mixture to avoid severe burns. Plant piping and similar equipment are also potential causes of burns.
- If hot asphalt cement contacts the skin, cool the contact ares with cold water but do not attempt to remove the asphalt. Contact the proper medical authority for care. The use of ice is not recommended.
- Do not place hot asphalt cement into a tank that has previously contained anything but an asphalt cement or a cut-back asphalt.

## Areas of Needed Research

The information reviewed in this search of the literature has revealed the following suggested areas of needed attention and research:

- The existing asphalt-related terminology used in North America is inconsistent with the terminology used elsewhere. For example, the term "asphalt" is often applied generically to petroleum derivatives, coal-tar derivatives, and mixtures of these derivatives with mineral aggregates. Consistent usage of terms could significantly reduce inherent confusion.
- Additional emissions sampling studies are needed to clearly assess the character and magnitude of both asphalt fumes generated in the paving industry and occupational respiratory exposures to these fumes.
- Sampling and analysis techniques should be consistent with standardized procedures that will allow representative comparisons can be made between the results from different asphalt materials and emissions investigations.
- This summary of health and safety practices is based on the identifiable English language reports up to the time of writing this report. Inclusion of the foreign language articles in Appendix B may add to the completeness of this

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# Figures and Tables

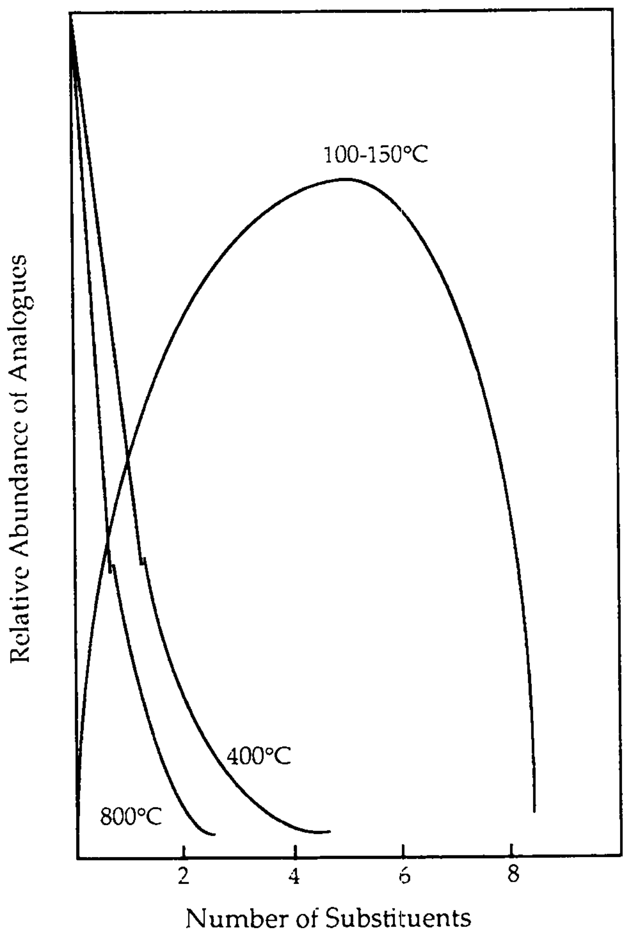


Figure 2.1. Correlation of temperature of formation with the relative abundance of substituted hydrocarbons (from Figure 2 in Cripps and Watkinson, 1978).

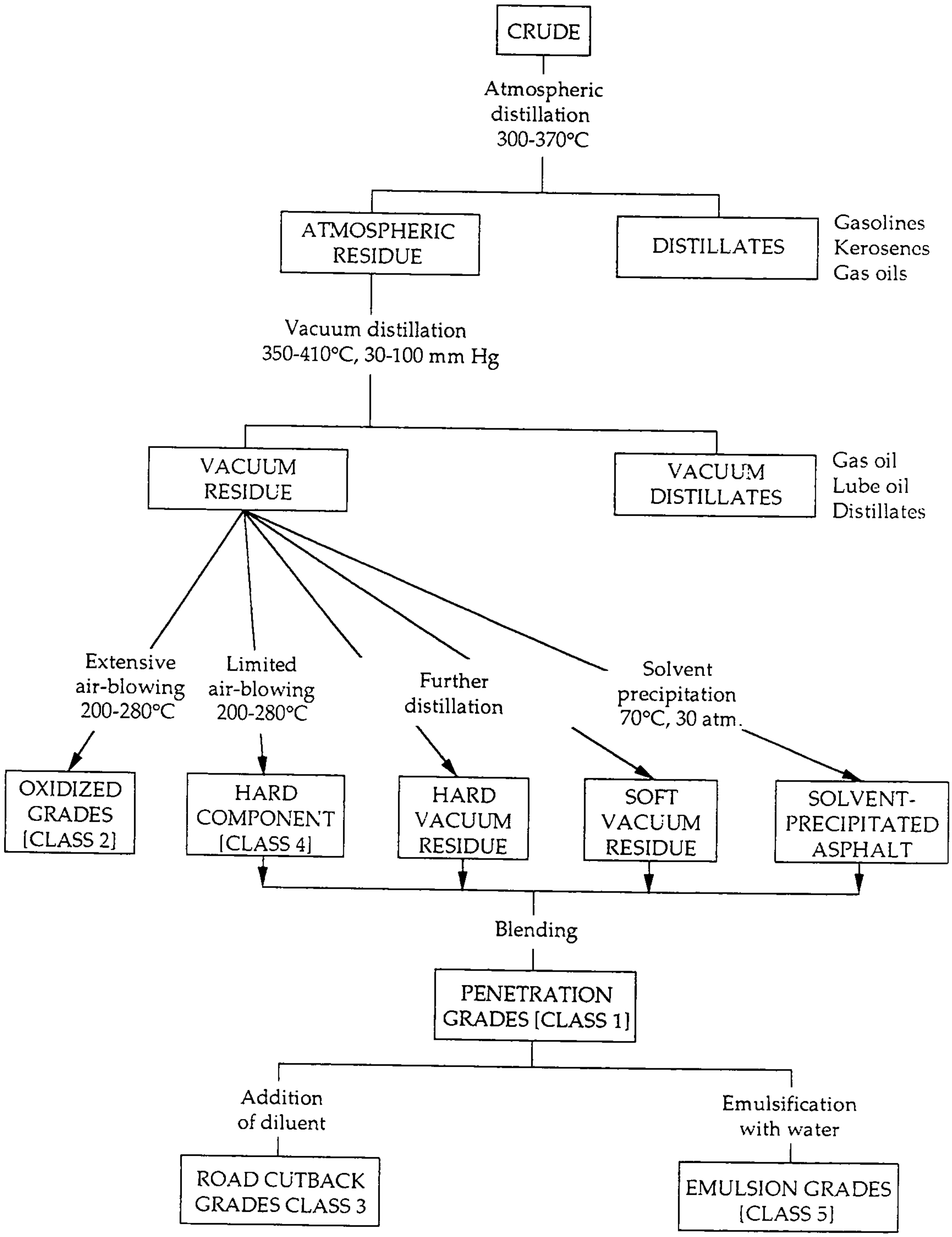


Figure 2.2 Main refining and processing methods in the production of asphalt (adapted from Figure 2 in IARC, 1985).

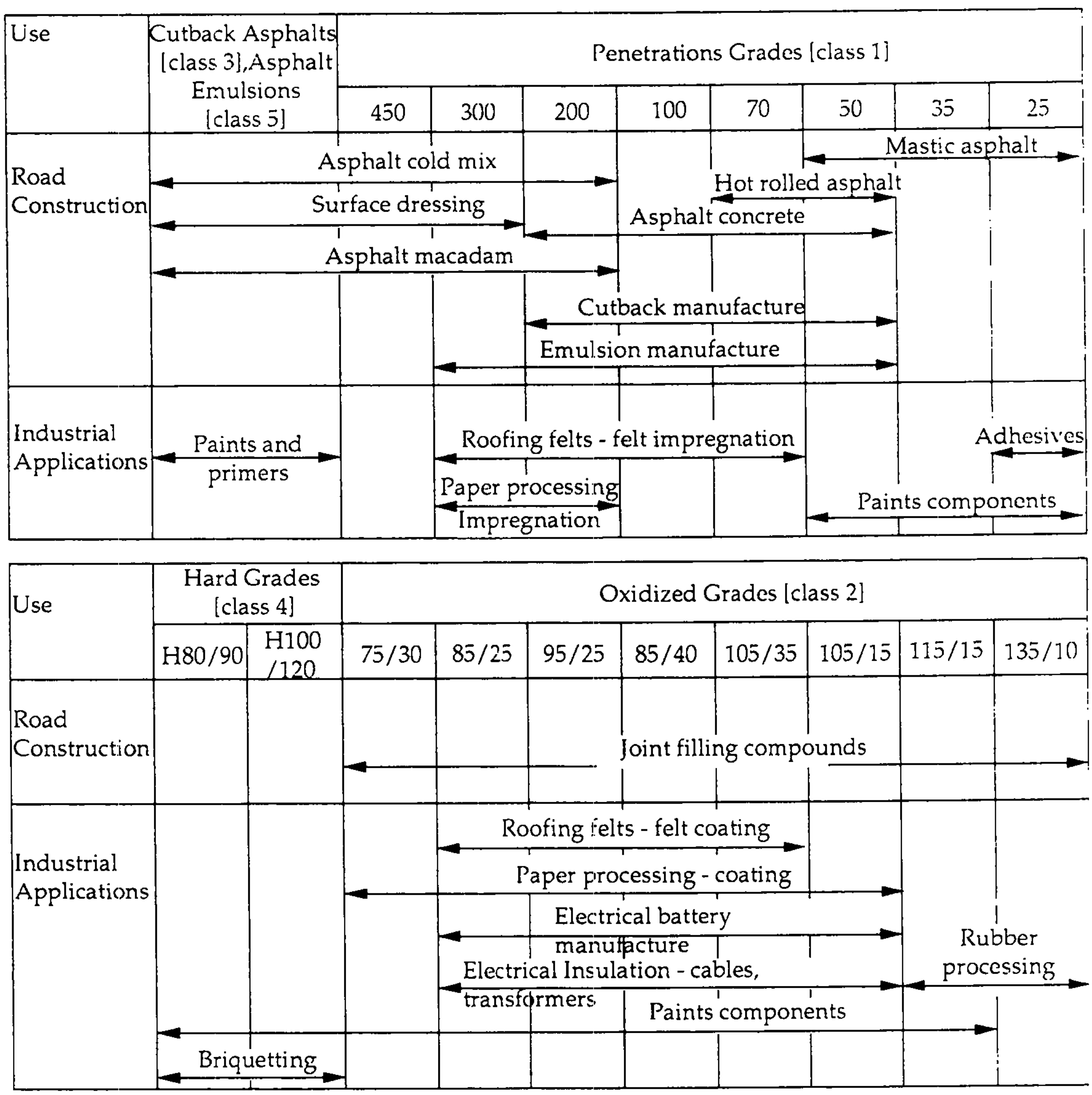


Figure 2.3 Principal uses of asphalt (adapted from Table 5 in IARC, 1985).

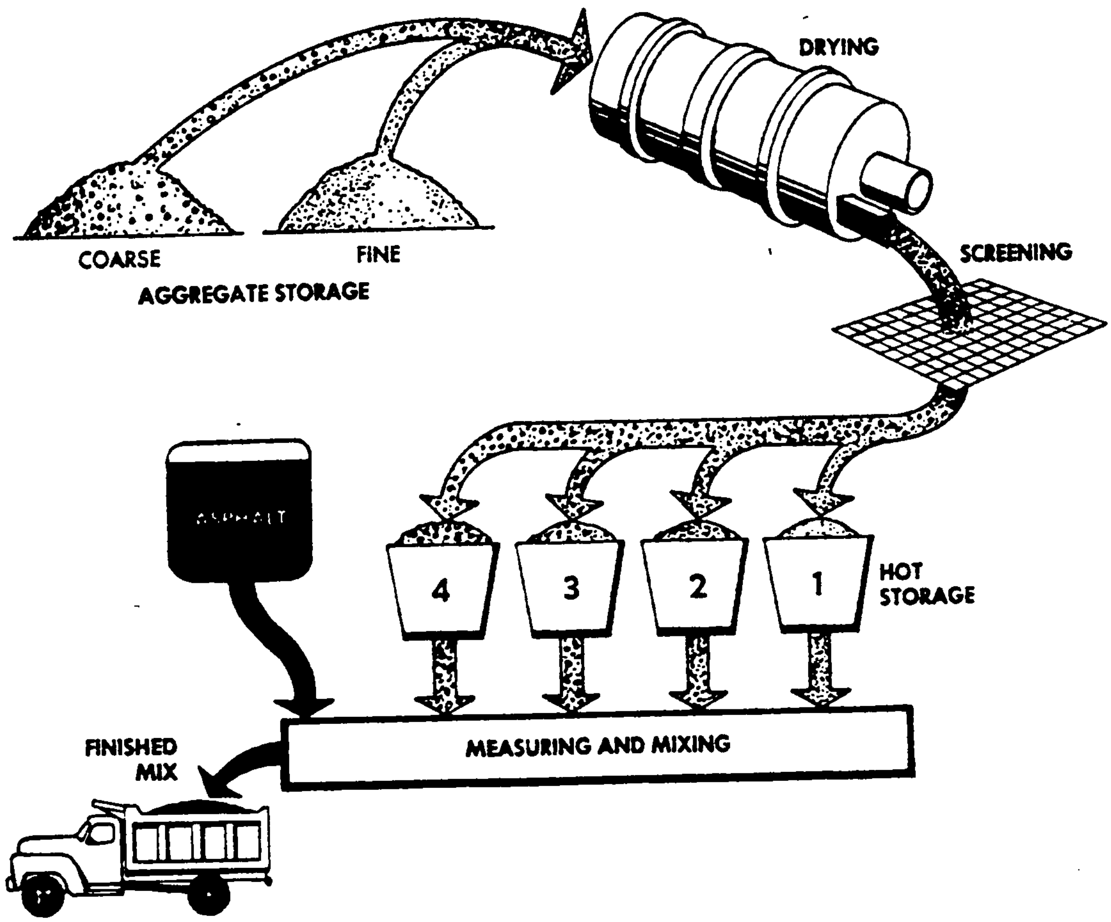


Figure 2.4 Typical diagram of batch or continuous asphalt plant (from Figure 1 in The Asphalt Institute, 1983).

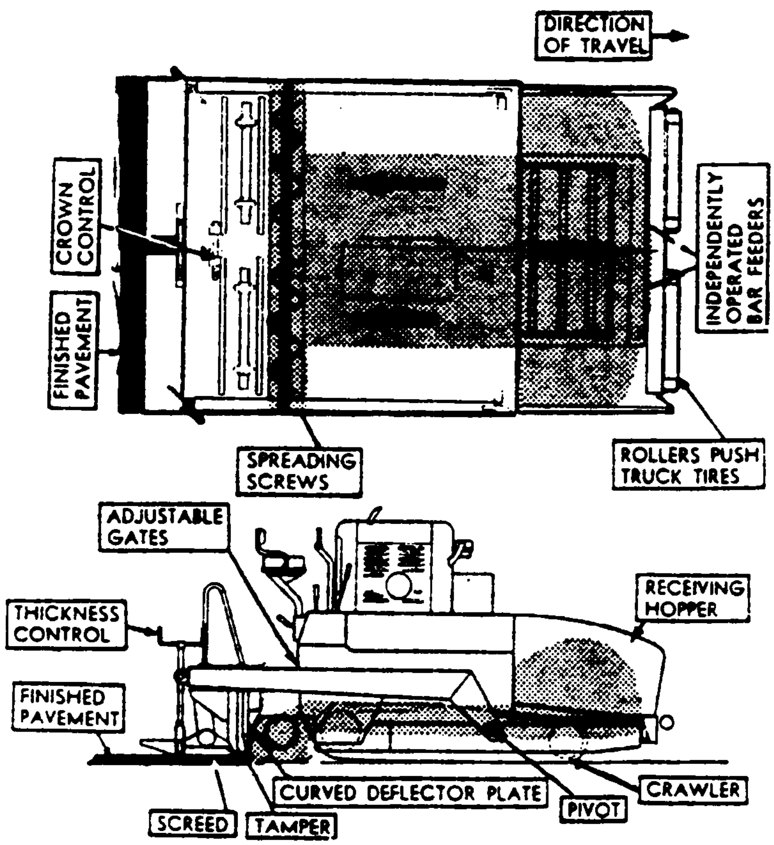


Figure 2.5 Flow of material through the asphalt paver (from Figure 1 in The Asphalt Institute, 1989a).

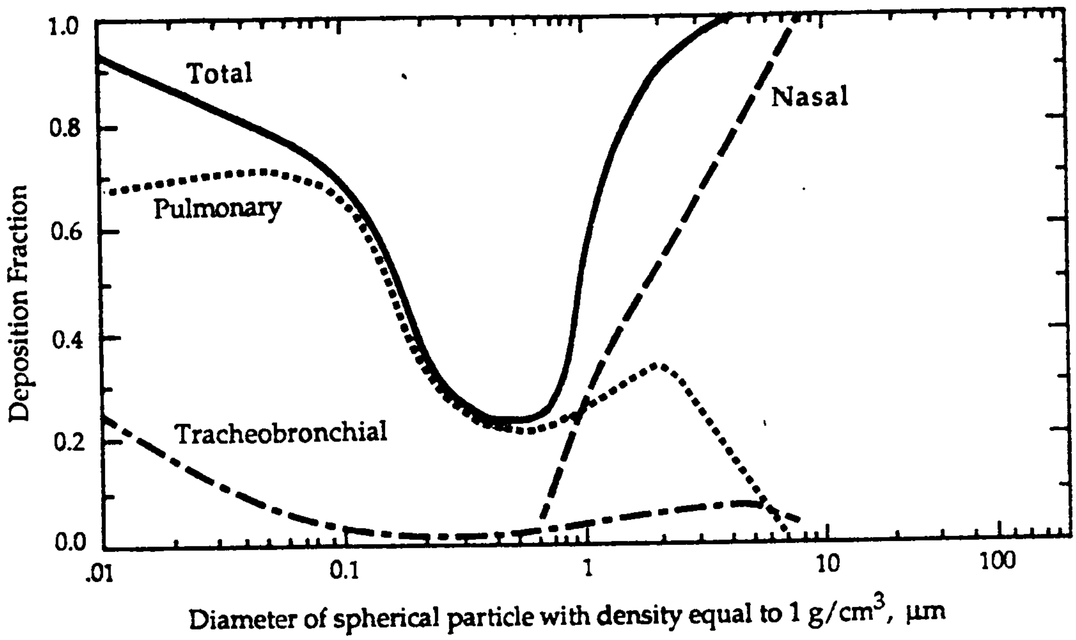


Figure 3.1. Deposition of inhaled particles in the total lung and in regional areas of the human lung (from Raabe, 1971).

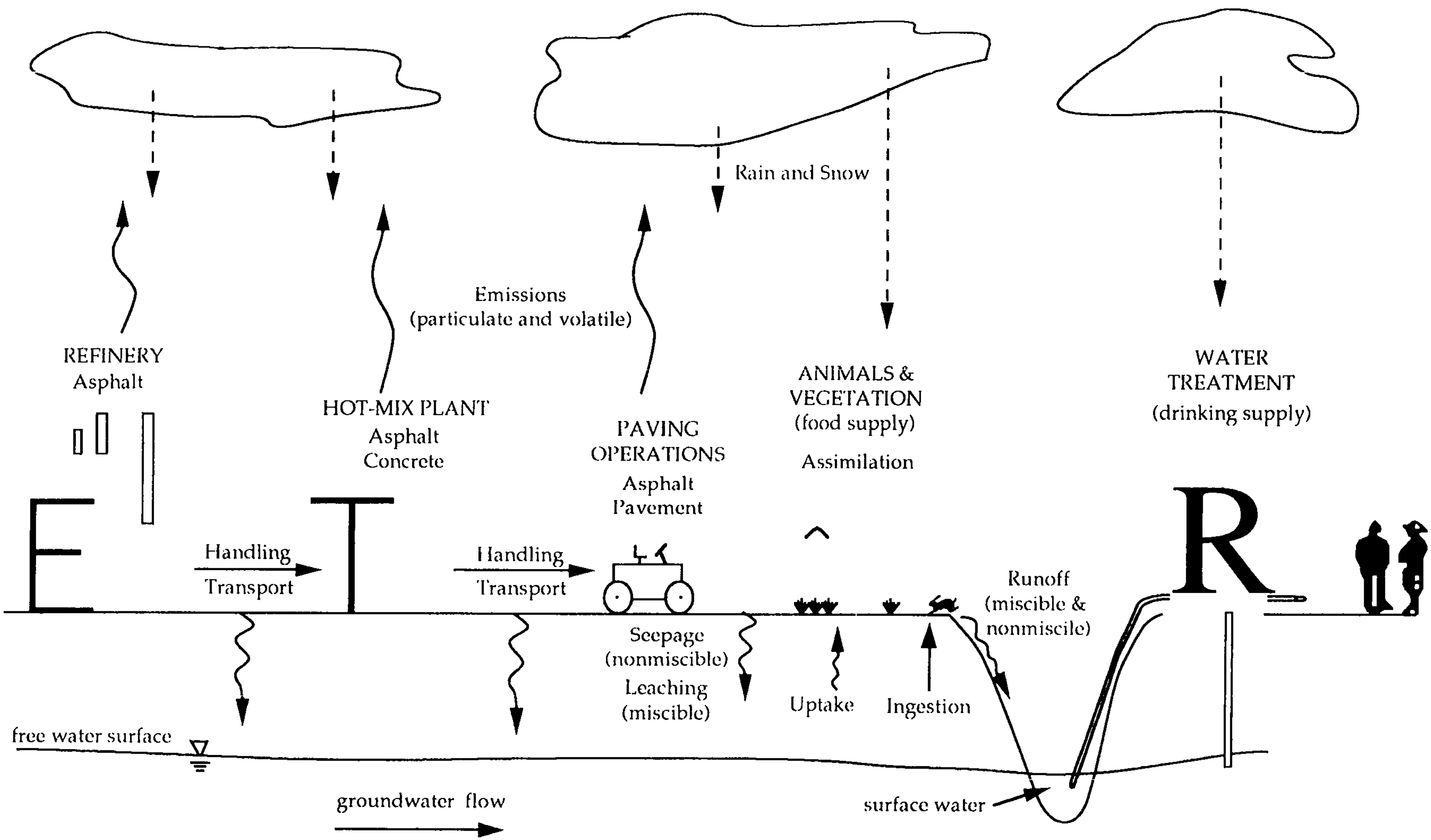


Figure 5.1 Potential exposure pathways of asphalt components to the environment and subseqent indirect exposure to man.

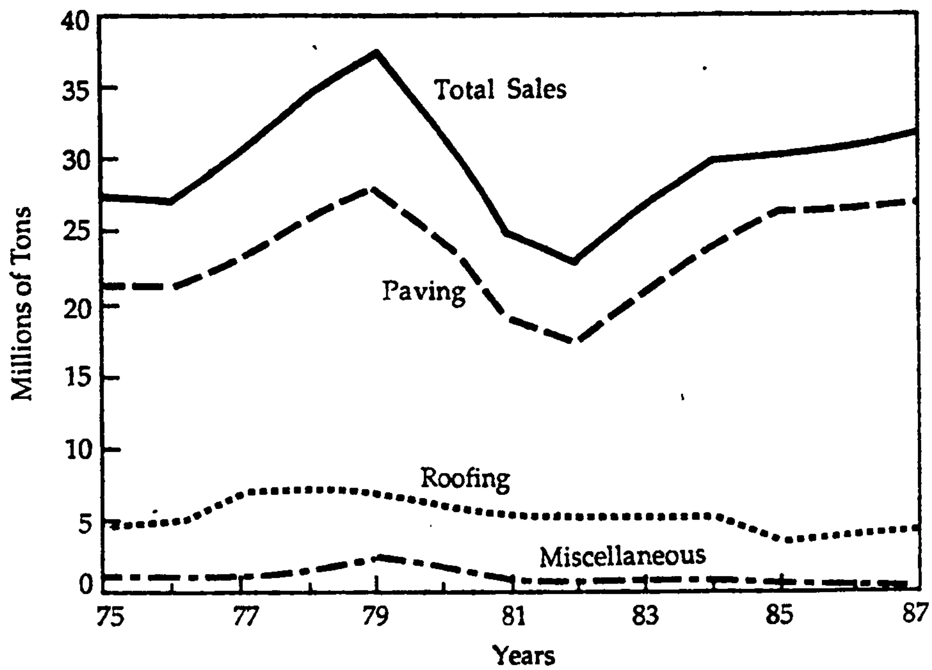


Figure 5.2 Annual sales of petroleum asphalt to domestic consumers in U. S. A. (from Figure 1.2 in The Asphalt Institute, 1989a).

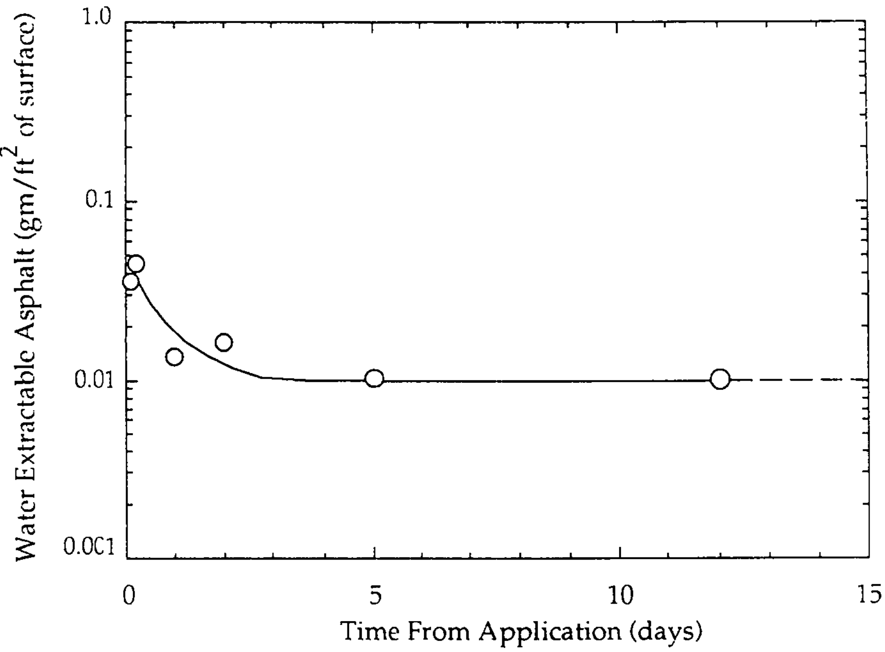


Figure 5.3 Area rainfall study: Comparison of areal leaching from hot-mix asphalt surface (adapted from Table 2 in Nielson et al., 1969).

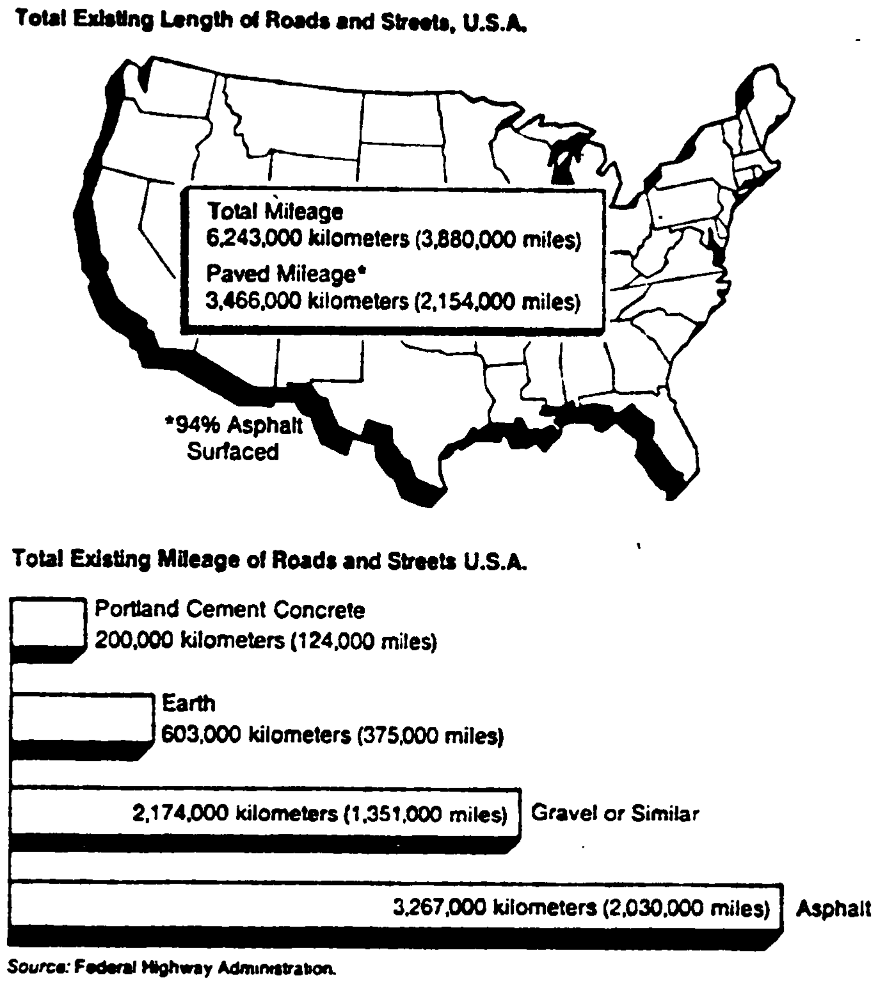


Figure 5.4 U. S. road mileage (from Figure 1.3 in The Asphalt Institute, 1989a).

Table 1.1
Overview of Strategic Highway Research Study (Adapted from Table 1.1 in Transportation Research Board, 1986).

| Research Area | Objective | Projected 5-Year Costs (S million) | Potential Results |
|---|---|---|---|
| Asphaltic Characteristics | Define chemical and physical characteristics of asphalt and their relationship to performance in pavement systems. | 50 | Better quality control and better materials; and improved design capability and performance predictions. Potential saving of S100 million per year. |
| Pavement Performance | Assess long-term performance of various pavements under various loading and environmental conditions. (Studies would continue for three additional 5-year terms of data collection and analysis.) | 50 | New capability to assess and select alternative pavement maintenance and rehabilitation strategies; and improved design and construction techniques. Potential saving of S10 billion. |
| Concrete and Structures | Understand chemical and physical phenomenon of hydration; evaluate new options such as recycled concrete and energy saving components; and develop nondestructive testing methods.<br><br>Develop new methods to stop further deterioration of existing chloride-contaminated bridge decks and other components. | 22 | Ability to produce a better quality and more durable concrete. Potential saving of S50 million per year.<br><br>More effective techniques for removing chloride from concrete or protecting concrete from chloride contamination. Potential saving of S400 million per year. |
| Highway Operations and Maintenance | Develop improved procedures for administering and controlling maintenance programs; develop new processes, equipment, and materials; and improve productivity of maintenance program.<br><br>Reduce the use of salt through management techniques and optimum use of mechanical or thermal removal plus alternative chemicals. | 28 | New management systems and increased maintenance productivity. Potential saving of S150 million per year.<br><br>Reduction in corrosion and environmental problems without a reduction in the level of service of snow and ice control programs. For example, potential savings from a decrease in automobile corrosion could be S45 million per year. |

Note: Subsequent to publication of the cited document, the six original research areas were consolidated into the four areas shown in this table.

Table 1.2
Computerized Databases Used to Identify References for the Summary of Health and Safety Practices.

- Cancerlit (National Library of Medicine; Bethesada, MD)
- CA Search (Chemical Abstracts Service; Columbus, OH)
- Chemical Abstracts (Chemical Abstracts Service; Columbus, OH)
- Compendex Plus (Engineering Information, Inc.; New York, NY)
- Dialog Homebase (Dialog Information Services, Inc.; Pal Alto, CA)
- Enviroline (R. R. Bowker Company; New York, NY)
- Federal Register Abstracts (National Standards Association; Gaithersburg, MD)
- Medline (National Library of Medicine; Bethesda, MD)
- NIOSH (National Institute for Occupational Safety and Health; Washington, DC)
- NTIS (National Technical Information Service; Springfield, VA)
- Pascal (Departement de l'Edition de l'Information Specialisee; Paris, France)
- P/E News (American Petroleum Institute; New York, NY)
- Pollution Abstracts (Cambridge Scientific Abstracts; Bethesda, MD)
- Toxline (National Library of Medicine; Bethesda, MD)
- TRIS (Transportation Research Board; Washington, D C)

Table 2.1
Typical Range in Content of Chemical Elements in Asphalt (adapted from text in IARC, 1985 and The Asphalt Institute, 1989b).

| Chemical Element | Typical Maximum | Typical Minimum |
|---|---|---|
| Carbon (%) | 95 | 75 |
| Hydrogen (%) | 15 | 8 |
| Nitrogen (%) | 3 | 0 |
| Oxygen (%) | 4 | 0 |
| Sulfur (%) | 10 | 2 |
| Vanadium (ppm) | 1200 | 30 |
| Nickel (ppm) | 150 | 0 |
| Iron (ppm) | 200 | 0 |

ppm, parts per million = µg/g.

Table 2.2
Typical Range in Content of the Generic Factions in Asphalt from ASTM D-4124 (adapted from text in IARC, 1985).

| Fraction | Typical Maximum | Typical Minimum |
|---|---|---|
| Asphaltenes (%) | 25 | 5 |
| Resins (%) | 25 | 15 |
| Cyclics (%) | 60 | 45 |
| Saturates (%) | 20 | 5 |

## Table 2.3
## Polynuclear Aromatic Hydrocarbons in Different Bitumens and Coal-Tar Pitches (from Table 1 in Wallcave et al., 1971).

| PAH Compound | Formula | Bitumen A | Bitumen B | Bitumen C | Bitumen D | Bitumen E | Bitumen F | Bitumen G | Bitumen H | Coal Tar Pitch A | Coal Tar Pitch B |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Anthracene | $C_{14}H_{10}$ | — | — | — | — | — | — | — | — | 8,600* | 10,000* |
| Phenanthrene | $C_{14}H_{10}$ | 2.3 (4.5) | 0.4 (7.5) | 3.5 (24) | 1.3 (62) | 0.6 (6.5) | 35* | 1.1 (6.3) | 2.3* | 31,000* | 29,000* |
| Pyrene | $C_{16}H_{10}$ | 0.6 (1.2) | 1.8 (18) | 4.0 (8.6) | 8.3 (34) | 0.9 (6.7) | 38 (89) | 0.3 (1.9) | 0.08 (0.8) | 20,000 (2,000) | 29,000 (2,400) |
| Fluoranthene | $C_{16}H_{10}$ | + | + | 2.0 (+) | + | + | 5 (+) | — | — | 40,000 (1,500) | 43,000 (1,400) |
| Benzofluorenes | $C_{17}H_{12}$ | + | + | + | + | + | + | + | | 7,300* | 5,100* |
| Benz[a]anthracene | $C_{18}H_{12}$ | 0.15 (1.1) | 2.1 (46) | 1.1 (6.9) | 0.7 (9.7) | 0.9 (13) | 35 (109) | 0.2 (1.2) | — (0.05) | 8,900 (1,500) | 12,500 (2,200) |
| Triphenylene | $C_{18}H_{12}$ | 0.25 (2.4) | 6.1 (31) | 3.1 (6.9) | 3.4 (8.5) | 3.8 (12) | 7.6 (43) | 1.0 (3.2) | 0.3 (0.7) | 1,500 (400) | 1,100 (600) |
| Chrysene | $C_{18}H_{12}$ | 0.2 (4.0) | 8.9 (101) | 2.3 (12) | 3.9 (31) | 3.2 (25) | 34 (158) | 0.7 (6.2) | 0.04 (0.4) | 7,400 (900) | 10,000 (2,700) |
| Benzo[a]pyrene | $C_{20}H_{12}$ | 0.5 (2.9) | 1.7 (12) | 1.3 (3.8) | 2.5 (7.2) | 1.6 (8.4) | 27 (69) | 0.1 (1.0) | — | 8,400 (1,500) | 12,500 (1,100) |
| Benzo[e]pyrene | $C_{20}H_{12}$ | 3.8 (11) | 13 (30) | 2.9 (5.5) | 3.2 (6.8) | 6.5 (24) | 52 (141) | 1.6 (4.1) | 0.03 (0.06) | 5,400 (600) | 7,000 (800) |
| Benzo [k]fluoranthene† | $C_{20}H_{12}$ | + (—) | —§ | + (—) | + (—) | + (—) | — | — | — | 7,100 (+) | 9,000 (+) |
| Perylene | $C_{20}H_{12}$ | — | 39 (9.7) | 2.2 (0.8) | 6.1 (2.0) | 2.9 (1.4) | 3.0 (—) | 0.1 (—) | — | 2,000 (+) | 3,300 (+) |
| Anthanthrene | $C_{22}H_{12}$ | — | Tr | Tr | Tr | + (—) | 1.8 (—) | — | — | 1,300 (+) | 2,100 (+) |
| Benzo[ghi]perylene | $C_{22}H_{12}$ | 2.1 (7.4) | 4.6 (9.6) | 1.0 (1.6) | 1.7 (2.9) | 2.7 (4.5) | 15 (41) | 0.6 (0.8) | Tr | 3,200 (+) | 3,300 (500) |
| Indeno[1,2,3-cd]pyrene | $C_{22}H_{12}$ | Tr | | Tr | Tr | Tr | 1.0 (—) | — | — | 7,300 (+) | 9,300 (+) |
| Picene | $C_{22}H_{14}$ | + | · | + | + | + | 1.0 (+) | + | — | NE | 2,000 (+) |
| Coronene | $C_{24}H_{12}$ | 1.9 (—) | 0.8 (0.5) | 0.5 (—) | 0.2 (—) | 0.9 (0.5) | 2.8 (1.9) | 0.9 ( ) | — | 700 (+) | 700 (+) |

All concentrations expressed in units of parts per million (ppm).
All concentrations represent an average of two analyses for each asphalt and each pitch sample.
Other polynuclear compounds, including some heterocyclic types, were found in low concentrations in certain asphalts and in the coal-tar pitches, but are not listed in this table. These include benzonaphthothiophenes, benzonaphthofuranes (brazans), benzacridines, and benzo[ghi]fluoranthene.

* Estimate includes alkyl derivatives.
† Benzo[b]fluoranthene usually associated with benzo[k]fluoranthene.
§ Contains benzo[b]fluoranthene.
Tr Trace
NE Not estimated but present in substantial amount.
\+ Not estimated but present in small amount.
— Not detected.
( ) Concentration of alkyl derivatives.

Table 2.4
Content of 14 Individual Polynuclear Aromatic Hydrocarbons in Some Penetration-Grade and Oxidized-Grade Asphalts (adapted from Tables 3.1 and 3.5 in Brandt et al., 1985).

| PAH | Penetration Grades | | | | Oxidized Grades | | |
|---|---|---|---|---|---|---|---|
| | 80/100 | 80/100 | 50/60 | 80/100 | 85/40 | 110/30 | 95/25 |
| Phenanthrene | 7.3 | 5.0 | 1.7 | 5.0 | 0.32 | 1.7 | 2.4 |
| Anthracene | 0.32 | 0.27 | 0.015 | 0.17 | 0.01 | 0.03 | 0.07 |
| Fluoranthene | 0.72 | 0.46 | 0.41 | 0.39 | 0.15 | 0.4 | 0.46 |
| Pyrene | 1.5 | 1.0 | 0.26 | 1.1 | 0.17 | 0.3 | 0.29 |
| Chrysene | 1.5 | 3.3 | 0.47 | 3.9 | 0.90 | 1.0 | 0.80 |
| Benz[a]anthracene | 1.1 | 0.89 | 0.14 | 0.63 | 0.33 | 0.3 | 0.23 |
| Perylene | 3.3 | 0.69 | 0.044 | 0.25 | 0.14 | 0.08 | 0.20 |
| Benzo[k]fluoranthene | 0.19 | ND | 0.024 | ND | 0.051 | 0.10 | 0.04 |
| Benzo[a]pyrene | 1.8 | 0.92 | 0.22 | 1.1 | 0.49 | 0.35 | 0.48 |
| Benzo[ghi]perylene | 4.2 | 2.3 | 1.67 | 2.7 | 1.3 | 1.2 | 2.0 |
| Anthanthrene | 0.11 | 0.04 | 0.006 | 0.02 | 0.01 | ND | 0.03 |
| Dibenzo[a,l]pyrene | ND | ND | ND | ND | ND | ND | ND |
| Dibenzo[a,i]pyrene | 0.50 | ND | 0.05 | 0.60 | ND | 0.3 | 0.10 |
| Coronene | ND | ND | 0.40 | ND | ND | ND | ND |

All concentrations in µg/g.
Asphalts were obtained from a range of crude oils originating from the Middle East, Venezuela and Mexico.
ND, not detected

Table 2.5
Carcinogenicity of Petroleum (from Table 3 in Binghan et al., 1976).

| Cocarcinogens | Carcinogens* | Inhibitors |
|---|---|---|
| Long-chain aliphatic and atomatic hydrocarbons (480-750°F)<br>Sulfur compounds | 4-5 ring aromatics (670-1000°F) | Cycloparaffins |

* Essential for the production of tumors.

Table 2.6
Relative Carcinogenicity of PAHs to Experimental Animals (adapted from Table 1 in Futoma et al., 1981; Table 1 in Gammage, 1983; Table 86 in Neff, 1979; Hites and Simonsick, Jr., 1987; Dias, 1987a; Dias, 1987b).

| Compound | Relative Carcinogenicity | Molecular Weight | No. of Rings |
|---|---|---|---|
| Naphthalene | — | 128 | 2 |
| 2-Methylnaphthalene | ± | 142 | 2 |
| Acenaphthene | — | 154 | 3 |
| 9H-Fluorene | — | 166 | 3 |
| Anthracene | — | 178 | 3 |
| Phenanthrene | — | 178 | 3 |
| Aceanthrylene | — | 202 | 4 |
| Fluoranthene | — | 202 | 4 |
| Pyrene | — | 202 | 4 |
| 11H-Benzo[a]fluorene | — | 216 | 4 |
| 11H-Benzo[b]fluorene | — | 216 | 4 |
| 7H-Benzo[c]fluorene | — | 216 | 4 |
| 2-Methylflouranthene | + | 216 | 4 |
| 3-Methylflouranthene | — | 216 | 4 |
| Benz[a]anthracene | + | 228 | 4 |
| Chrysene | ± | 228 | 4 |
| Naphthacene | — | 228 | 4 |
| Triphenylene | — | 228 | 4 |
| 3-Methylchrysene | ++ | 242 | 4 |
| 5-Methylchrysene | +++ | 242 | 4 |
| 7,12-Dimethylbenz[a]anthracene | ++++ | 256 | 4 |
| Benzo[a]phenanthrene | +++ | 228 | 5 |
| Benzo[c]phenanthrene | +++ | 228 | 5 |
| Benz[j]aceanthrylene (cholanthrene) | ++ | 252 | 5 |
| Benzo[b]fluoranthene | ++ | 252 | 5 |
| Benzo[j]fluoranthene | ++ | 252 | 5 |
| Benzo[k]fluoranthene | — | 252 | 5 |
| Benzo[mno]fluoranthene | — | 252 | 5 |
| Benzo[a]pyrene | +++ | 252 | 5 |
| Benzo[e]pyrene | — | 252 | 5 |
| Perylene | — | 252 | 5 |
| 13H-Dibenzo[ac]fluorene | ± | 266 | 5 |
| 13H-Dibenzo[ag]fluorene | + | 266 | 5 |
| 13H-Dibenzo[ah]fluorene | ± | 266 | 5 |
| 3-Methylcholanthrene | ++++ | 266 | 5 |
| Dibenz[ac]anthracene | + | 278 | 5 |
| Dibenz[ah]anthracene | +++ | 278 | 5 |
| Dibenz[aj]anthracene | + | 278 | 5 |
| Picene | + | 278 | 5 |
| Benzo[ghi]perylene | — | 276 | 6 |
| Dibenzo[def,mno]chrysene (anthanthrene) | — | 276 | 6 |
| Indeno[1,2,3-cd]pyrene | + | 276 | 6 |
| Dibenzo[b,def]chrysene (dibenzo[a,h]pyrene) | +++ | 302 | 6 |
| Dibenzo[def,p]chrysene (debenzo[a,l]pyrene) | + | 302 | 6 |
| Benzo[rst]pentaphene (dibenzo[a,i]pyrene) | +++ | 302 | 6 |
| Coronene | — | 300 | 7 |

Notation: — Not Active, + Weakly active, ++ Moderately active, +++ Very active, ++++ Extremely active, ± Uncertain.
Alternate compound name in parentheses.
This list contains commonly characterized compounds and does not represent a complete list of known PAHs.

Table 3.1
National Occupational Exposure Limits for Asphalt Fumes, Particulate PAHs, and Benzo[a]pyrene (from American Conference of Governmental Industrial Hygienists, Inc., 1980, 1984; International Labor office, 1980; National Institute for Occupational Safety and Health, 1977; Occupational Safety and Health Administration, 1988).

| Country | Asphalt Fumes | Polynuclear Aromatic Hydrocarbons (Particulate) | Benzo[a]pyrene | Interpretation | Status |
|---|---|---|---|---|---|
| Australia | 5 | 0.2 | | TWA | Guideline |
| Belgium | 5 | 0.2 | | TWA | Regulation |
| Italy | 5 | | | TWA | Guideline |
| Netherlands | 5 | 0.2 | | TWA | Guideline |
| Sweden | | | 0.01 | TWA | Guideline |
| Switzerland | 5 | | | TWA | Regulation |
| USSR | | | 0.00015 | Maximun | Regulation |
| USA - ACGIH | 5 | 0.2 | | TWA | Guideline |
| | 10 | | | STEL | Guideline |
| - NIOSH | 5 | | | Ceiling (15min) | Guideline |
| - OSHA | 5 | | | TWA | Regulation* |

All Concentrations in units of mg/m$^3$.
* Proposed regulation
TWA, time-weighted average (8 hour).
STEL, short-term exposure limit.

Table 3.2
Particle Size Distribution Measured During Refinery Road-Tanker Loading (adapted from Table 1.2 in Brandt,et al., 1985).

| Particle Size (μm) | Percent Mass |
|---|---|
| < 12.5 | 99.1 |
| < 3.8 | 82 |
| < 1.2 | 5 |

Table 3.3
Summary of Personal Exposure During Refinery Road-Tanker Loading (adapted from Tables 2.2, 2.3, and 2.5 in Brandt et al., 1985).

| Duties | Total Particulate Matter (TPM) | | | | | Benzene Soluble Matter (BSM) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | TWA (8h) | | | | TWA (8h) | | BSM as % TPM | |
| | No. of Samples | Avg. Conc. | Range | Avg. Conc. | Range | No. of Samples | Avg. Conc. | Avg. Conc. | Range | Avg. | Range |
| Loading | 2 | 2.2 | — | 1.9 | — | 2 | 0.7 | 0.7 | — | 32 | — |
| Various | 2 | 1.0 | — | 0.8 | — | 2 | 0.1 | 0.1 | — | 10 | — |
| Total | 4 | — | 0.9-3.2 | 1.4 | 0.7-2.9 | 4 | — | 0.4 | < 0.1-1.0 | — | 10-34 |

All concentrations are expressed in units of $mg/m^3$.
— Values were not reported by the authors.

Table 3.4
Average PAH Concentrations in Fumes Collected During Refinery Road-Tanker Loading (adapted from Tables 2.4 and 2.5 in Brandt et al., 1985).

| Compound | No. of Rings | Conc. in BSM (μg/g) Avg. | Conc. in BSM (μg/g) min-max | TWA (8h) ($\mu g/m^3$) Avg. | TWA (8h) ($\mu g/m^3$) min-max |
|---|---|---|---|---|---|
| Phenanthrene | 3 | 27 | nd-90 | — | — |
| Anthracene | 3 | nd | nd | — | — |
| Fluoranthene | 4 | 0.5 | nd-2 | — | — |
| Pyrene | 4 | 4.8 | nd-16 | — | — |
| Chrysene | 4 | 15 | 7.0-28 | — | — |
| Benzo[a]anthracene | 4 | 7.5 | 1.6-18 | — | — |
| Perylene | 5 | 4.6 | 2.2-8.8 | — | — |
| Benzo[k]fluoranthene* | 5 | 5.6 | 3.5-11 | — | — |
| Benzo[a]pyrene | 5 | 15 | 7.3-25 | — | — |
| Benzo[g,h,i]perylene | 6 | 25 | 10-51 | — | — |
| Anthanthrene | 6 | 0.4 | nd-1.4 | — | — |
| Dibenzo[a,l]pyrene/ Dibenzo[a,i]pyrene | 6 | nd | nd | — | — |
| Sum 11 (4-,5- and 6-ring) PAH | | 78 | 38-95 | 33 | 3.8-95 |
| Coronene | 7 | nd | nd | — | — |

All concentrations were obtained from 4 personal samples.
nd Non-detectable.
— Values were not reported by the authors.
* This compound was originally reported as a second citation of Benzo[a]anthracene in Table 2.4 of Brandt, et. al. (1985). Scrutiny of Table 1.1 in that article indicated that Benzo[k]fluoranthene is the correct compound that represents this data.

## Table 3.5
## Composition of Fugative Asphalt Hot-Mix Emissions (from Table V in Puzinauskas and Corbett, 1975).

| Sample Location | Edison, N.J. | Greensboro, N.C. |
|---|---|---|
| Number of Samples | 6 | 2 |
| **Non-visible Components (ppm)** | | |
| Carbon monoxide (CO) | 4-6 | 3-4 |
| Nitrogen dioxide ($NO_2$) | <0.1 | 0.05-0.08 |
| Sulfur dioxide ($SO_2$) | <2 | <0.05 |
| Hydrogen sulfide ($H_2S$) | <0.2-1.5 | <0.2 |
| Carbonyl sulfide (COS) | <0.2 | <0.2 |
| Mercaptan (RSH) | <0.2 | <0.2 |
| Aldehydes (RCHO) | <0.1 | 0.3-0.4 |
| Phenol (OOH) | <1 | <1 |
| Ozone ($O_3$) | <0.1 | — |
| Methane ($CH_4$) | 2-3 | 2-3 |
| Non-methane Hydrocarbons ($C_2$ -$C_6$ ) | <1 | <1 |
| Volatile organic compounds ($C_7$-$C_{14}$ ) | 0.5-1.5 | 0.5-1.0 |
| **Particulates ($mg/m^3$)** | | |
| Total particulates | 2.6-7.2 | 0.5-5.7 |
| Benzene solubles | 0.3-2.8 | 0.2-5.4 |
| Polynuclear aromatics (total) max. | 0.00034 | 0.00016 |
| Nickel (Ni) max | 0.000005 | 0.00004 |
| Vanadium (V) max | 0.00008 | <0.0001 |
| Cadmium (Cd) | — | <0.00005 |
| Lead (Pb) | — | <0.00005 |

NOTE: Where the less than (<) values are indicated, the numbers represent the sensitivity of the sampling and testing procedures used.

Table 3.6
Polynuclear Aromatic Hydrocarbons in Sampled Particulates from Fugitive Asphalt Hot-Mix Emissions (from Table VI in Puzinauskas and Corbett, 1975).

| Sampling Sites | Edison, N.J. | | Greensboro, N. C. | |
|---|---|---|---|---|
| Number of Samplings | 6 | | 2 | |
| Compound | Range | Avg. | Range | Avg. |
| Pyrene | 44-240 | 107 | — | 96 |
| Benz[a]anthracene | 5-24 | 11 | 32-38 | 35 |
| Benzo[a]pyrene | 3-20 | 11 | 14-22 | 18 |
| Benzo[e]pyrene | 14-40 | 26 | ND | |
| Perylene | 5-16 | 12 | — | 6 |

All concentrations are expressed in units of $\mu g/1000\ m^3$ of gas.
ND Not detected
— Values were not reported

Table 3.7
Asphalt Fume Sampling Around Transport Vehicles During Hot-Mix* Loading Operations: Florida Sampling (from Table 4.1 in NAPA, 1989).

| PAH mg/m³ | Truck in morning (4 hrs) Left Front | Left Rear | Right Rear | Truck in afternoon (5 hrs) Left Front | Left Rear | Right Rear |
|---|---|---|---|---|---|---|
| Acenaphthene | BMDL | BMDL | BMDL | BMDL | BMDL | BMDL |
| Acenaphthylene | BMDL | BMDL | BMDL | BMDL | BMDL | BMDL |
| Anthracene | BMDL | BMDL | BMDL | BMDL | BMDL | BMDL |
| Benzo[a]anthracene | BMDL | BMDL | BMDL | BMDL | BMDL | BMDL |
| Benzo[b]fluoranthene | BMDL | BMDL | BMDL | BMDL | BMDL | BMDL |
| Benzo[k]fluoranthene | BMDL | BMDL | BMDL | BMDL | BMDL | BMDL |
| Benzo[g,h,i]perylene | BMDL | BMDL | BMDL | BMDL | BMDL | BMDL |
| Benzo[a]pyrene | BMDL | BMDL | BMDL | BMDL | BMDL | BMDL |
| Benzo[e]pyrene | BMDL | BMDL | BMDL | BMDL | BMDL | BMDL |
| Chrysene | BMDL | BMDL | BMDL | BMDL | BMDL | BMDL |
| Dibenzo[a, h]anthracene | BMDL | BMDL | BMDL | BMDL | BMDL | BMDL |
| Fluoranthene | BMDL | BMDL | BMDL | BMDL | BMDL | BMDL |
| Fluorene | BMDL | BMDL | BMDL | BMDL | BMDL | BMDL |
| Indeno[1, 2, 3-cd]pyrene | BMDL | BMDL | BMDL | BMDL | BMDL | BMDL |
| Naphthalene | BMDL | BMDL | BMDL | BMDL | BMDL | BMDL |
| Phenanthrene | BMDL | BMDL | BMDL | BMDL | BMDL | BMDL |
| Pyrene | BMDL | BMDL | BMDL | BMDL | BMDL | BMDL |
| Particulate filter analysis, mg/m³ | | | | | | |
| Particulate mass | 2.663 | 1.922 | 2.387 | 3.766 | 3.484 | 4.174 |
| Benzene soluble organics mass | BMDL | BMDL | BMDL | BMDL | BMDL | BMDL |

* AC-30 paving asphalt.
BMDL = Below the method detection limit.

Table 3.8
Asphalt Fume Sampling Around Transport Vehicles During Hot-Mix* Loading Operations: Maryland Sampling (from Table 4.4 in NAPA, 1989).

| PAH $mg/m^3$ | Eight Hours of Testing A | B | C |
|---|---|---|---|
| Acenaphthene | BMDL | BMDL | BMDL |
| Acenaphthylene | BMDL | BMDL | BMDL |
| Anthracene | BMDL | BMDL | BMDL |
| Benzo[a]anthracene | BMDL | BMDL | BMDL |
| Benzo[b]fluoranthene | BMDL | BMDL | BMDL |
| Benzo[k]fluoranthene | BMDL | BMDL | BMDL |
| Benzo[g,h,i]perylene | BMDL | BMDL | BMDL |
| Benzo[a]pyrene | BMDL | BMDL | BMDL |
| Benzo[e]pyrene | BMDL | BMDL | BMDL |
| Chrysene | BMDL | BMDL | BMDL |
| Dibenzo[a, h]anthracene | BMDL | BMDL | BMDL |
| Fluoranthene | BMDL | BMDL | BMDL |
| Fluorene | BMDL | BMDL | BMDL |
| Indeno[1, 2, 3-cd]pyrene | BMDL | BMDL | BMDL |
| Naphthalene | BMDL | BMDL | BMDL |
| Phenanthrene | BMDL | BMDL | BMDL |
| Pyrene | BMDL | BMDL | BMDL |
| Particulate filter analysis, $mg/m^3$ | | | |
| Particulate mass | 0.335 | 0.189 | 0.721 |
| Benzene soluble organics mass | 0.348 | 0.161 | 0.154 |

* AC-20 paving asphalt.
BMDL = Below the method detection limit.

Table 3.9
Worker Exposure to Particulates in Asphalt Paving Emissions (from Table 3 in Puzinauskas, 1980).

| Worker | Test No. | Sampling Time (min) | Sample Volume (liters) | Mass of Particulates (mg) | Concentration of Particulates (mg/m$^3$) |
|---|---|---|---|---|---|
| Paver Operatior | 1* | 86 | 261 | 0.040 | 0.15 |
| | 2* | 218 | 698 | 1.330 | 1.90 |
| | 3 | 116 | 370 | 0.200 | 0.54 |
| | 4 | 168 | 507 | 1.495 | 2.94 |
| | 5 | 217 | 718 | 0.655 | 0.91 |
| | 6* | 90 | 275 | 0.310 | 1.03 |
| | 7* | 61 | 188 | 0.060 | 0.32 |
| | 8 | 157 | 458 | 0.415 | 0.91 |
| | 9* | 85 | 294 | 0.080 | 0.27 |
| | 10 | 80 | 278 | 1.560 | 5.61 |
| | 11 | 91 | 315 | 0.135 | 0.43 |
| | 12 | 123 | 370 | 0.495 | 1.34 |
| | 13* | 77 | 270 | 0.155 | 0.57 |
| | 14 | 178 | 620 | 0.375 | 0.60 |
| Raker | 1* | 98 | 319 | 0.235 | 0.74 |
| | 2* | 179 | 522 | 1.805 | 3.46 |
| | 3 | 116 | 346 | 0.150 | 0.43 |
| | 4 | 178 | 556 | 0.195 | 0.35 |
| | 5 | 212 | 633 | 0.160 | 0.25 |
| | 6* | 104 | 349 | 0.295 | 0.84 |
| | 7* | 62 | 209 | 0.085 | 0.41 |
| Screedman | 8 | 156 | 594 | 0.535 | 0.90 |
| | 9* | 85 | 258 | 0.085 | 0.33 |
| | 10 | 75 | 229 | 0.200 | 0.87 |
| | 11 | 86 | 261 | 0.090 | 0.34 |
| | 12 | 118 | 409 | 0.365 | 0.89 |
| | 13* | 75 | 230 | 0.230 | 1.00 |
| | 14 | 178 | 530 | 0.780 | 1.47 |

No dust observed during sampling.
* Substantial airborne mineral dust observed during construction operations.

Table 3.10
PAH Concentrations Found In The Working Atmosphere During Paving Operations (from Table 2 in Malaiyandi et al., 1982).

| PAH | PAH Concentration (μg/m$^3$) | | | | | |
|---|---|---|---|---|---|---|
| | Site I | | | Site II | | |
| | Ambient Air | Machine Driver | Level Wheel Operator | Ambient Air | Machine Driver | Level Wheel Operator |
| Fluoranthene | 1.190 | INT* | 0.92 | 0.48 | 0.78 | 0.91 |
| Pyrene | 0.51 | 0.85 | 0.51 | 0.04 | 2.14 | 0.33 |
| Benz[a]anthracene | 0.23 | 6.59 | 3.79 | 0.03 | 8.78 | 2.25 |
| Chrysene | 0.19 | 2.49 | 0.19 | 0.10 | 1.05 | 0.71 |
| Dimethylbenz[a]anthracene | 0.01 | 0.02 | 0.07 | ND* | 0.14 | 0.03 |
| Perylene | 0.01 | 0.06 | Trace | 0.01 | Trace | 0.01 |
| Benzo[k]fluoranthene | 0.01 | 0.03 | 0.01 | 0.01 | 0.05 | 0.01 |
| Benzo[a]pyrene | Trace | 0.02 | 0.01 | Trace | Trace | 0.01 |
| Benzo[g,h,i]perylene | 0.04 | 0.10 | 0.03 | 0.03 | 0.03 | 0.03 |
| Dibenz[a,h]anthracene | 0.01 | Trace | 0.01 | ND | 0.01 | 0.01 |
| Indeno[1,2,3-cd]pyrene | 0.01 | 0.04 | 0.03 | 0.01 | 0.01 | 0.01 |
| Total PAH | 2.21 | 10.20 | 5.57 | 0.71 | 12.99 | 4.32 |
| Volume of Air Samples (Litres) | 740 | 580 | 580 | 870 | 870 | 870 |

* INT - Interference
* ND - Not Determined

Table 3.11
Summary of Personal Exposure During Road Surfacing (adapted from Tables 2.2, 2.3, and 2.5 in Brandt et al., 1985).

| Duties | Total Particulate Matter (TPM) | | | | | Benzene Soluble Matter (BSM) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | No. of Samples | Concentration Avg. | Concentration Range | TWA (8h) Avg. | TWA (8h) Range | No. of Samples | Conc. Avg. | TWA (8h) Avg. | TWA (8h) Range | % TPM Avg. | % TPM Range |
| Paver Driver | 2 | 0.6 | — | 0.3 | — | 2 | 0.1 | 0.1 | — | 17 | — |
| Chipper Driver | 1 | 15.1 | — | 15.1 | — | 1 | 0.1 | 0.1 | — | 0.1 | — |
| Raker | 3 | 1.2 | — | 1.2 | — | 3 | 0.1 | 0.1 | — | 8* | — |
| Operation 1 | 4 | — | 0.6-15.1 | — | 0.6-15.1 | 4 | — | — | — | — | 0.5-36 |
| Operation 2 | 2 | — | 0.2-0.4 | — | 0.2-0.4 | 2 | — | — | — | — | 6-51 |

All concentrations are expressed in units of $mg/m^3$.
— Values were not reported by the authors.
* This value was originally reported in Table 2.2 of Brandt, et. al. (1985) as 0.1, which represents an incorrect numerical computation of the data.

Table 3.12
Personal Sampling of Asphalt Paving Crew Members: Florida Sampling* (from Table 4.2 in NAPA, 1989).

| Substance($mg/m^3$) | Screedman (smoker) | Luteman (smoker) | Paver Operator | Screedman | Roller Operator |
|---|---|---|---|---|---|
| Resin filter analysis | | | | | |
| Acenaphthene | BMDL | BMDL | BMDL | BMDL | BMDL |
| Acenaphthylene | 0.00852 | 0.00209 | 0.00389 | 0.00603 | BMDL |
| Anthracene | BMDL | BMDL | BMDL | 0.00065 | BMDL |
| Benzo[a]anthracene | 0.00019 | BMDL | BMDL | BMDL | BMDL |
| Benzo[b]fluoranthene | 0.00009 | BMDL | BMDL | BMDL | BMDL |
| Benzo[k]fluoranthene | BMDL | BMDL | BMDL | BMDL | BMDL |
| Benzo[g,h,i]perylene | BMDL | BMDL | BMDL | BMDL | BMDL |
| Benzo[a]pyrene | 0.000019 | 0.00007 | BMDL | BMDL | BMDL |
| Benzo[e]pyrene | BMDL | BMDL | BMDL | BMDL | BMDL |
| Chrysene | BMDL | BMDL | BMDL | BMDL | BMDL |
| Dibenzo[a, h]anthracene | BMDL | BMDL | 0.00019 | 0.00017 | BMDL |
| Fluoranthene | 0.00152 | 0.00042 | 0.00097 | 0.00138 | BMDL |
| Fluorene | BMDL | 0.00056 | BMDL | BMDL | BMDL |
| Indeno[1, 2, 3-cd]pyrene | 0.01042 | BMDL | BMDL | BMDL | BMDL |
| Naphthalene | 0.00748 | 0.00695 | 0.00583 | 0.00948 | BMDL |
| Phenanthrene | BMDL | 0.00188 | 0.00544 | 0.00629 | BMDL |
| Pyrene | BMDL | 0.00056 | 0.00078 | 0.00155 | BMDL |
| Total PAH** | 0.02841 | 0.01253 | 0.01710 | 0.02585 | — |
| Particulate filter analysis | | | | | |
| Particulate mass | 0.218 | 0.160 | 1.079 | 0.215 | 0.477 |
| Benzene soluble organics mass | 0.114 | BMDL | BMDL | 0.129 | BMDL |

* AC-30 paving asphalt.
** Includes only those substances for which concentrations were found to be above the method detection limits.
BMDL = Below the method detection limit.

Table 3.13
Personal Sampling of Asphalt Paving Crew Members: Maryland Sampling* (from Table 4.5 in NAPA, 1989).

| Substance, $mg/m^3$ | Screedman (right) | Luteman | Paver Operator | Screedman (smoker) | Roller Operator |
|---|---|---|---|---|---|
| Resin filter analysis | | | | | |
| Acenaphthene | BMDL | BMDL | BMDL | BMDL | BMDL |
| Acenaphthylene | BMDL | BMDL | BMDL | BMDL | BMDL |
| Anthracene | BMDL | BMDL | BMDL | BMDL | BMDL |
| Benzo[a]anthracene | BMDL | BMDL | BMDL | BMDL | BMDL |
| Benzo[b]fluoranthene | BMDL | BMDL | BMDL | BMDL | BMDL |
| Benzo[k]fluoranthene | BMDL | BMDL | BMDL | BMDL | BMDL |
| Benzo[g,h,i]perylene | BMDL | BMDL | BMDL | BMDL | BMDL |
| Benzo[a]pyrene | BMDL | BMDL | BMDL | BMDL | BMDL |
| Benzo[e]pyrene | BMDL | BMDL | BMDL | BMDL | BMDL |
| Chrysene | BMDL | BMDL | BMDL | BMDL | BMDL |
| Dibenzo[a, h]anthracene | BMDL | BMDL | BMDL | BMDL | BMDL |
| Fluoranthene | BMDL | BMDL | BMDL | BMDL | BMDL |
| Fluorene | 0.00081 | 0.00038 | 0.00236 | 0.00039 | BMDL |
| Indeno[1, 2, 3-cd]pyrene | BMDL | BMDL | BMDL | BMDL | BMDL |
| Naphthalene | 0.00375 | 0.00272 | 0.00700 | 0.00334 | BMDL |
| Phenanthrene | BMDL | BMDL | BMDL | BMDL | BMDL |
| Pyrene | BMDL | BMDL | BMDL | BMDL | BMDL |
| Total PAH** | 0.00456 | 0.00310 | 0.00936 | 0.00373 | — |
| Particulate filter analysis | | | | | |
| Particulate mass | 0.441 | 0.324 | 0.903 | 0.143 | 0.330 |
| Benzene soluble organics mass | 0.406 | 0.376 | 0.756 | 0.197 | 0.098 |

* AC-20 paving asphalt.
** Includes only those substances for which concentrations were found to be above the method detection limit.
BMDL = Below the method detection limit.

Table 3.14
Environmental and Biological Monitoring of Asphalt Hot-Mix Paving Operations (adapted from Table 2 in Sforzolini et al., 1986).

| Monitoring Approach | Results |
|---|---|
| ENVIRONMENTAL | |
| Materials | |
| Mutagenicity[a] | Negative |
| Total PAH[b] | 190 (μg/g) |
| Benzo[a]pyrene[b] | 8 (μg/g) |
| Air Samples | |
| Mutagenticity | Negative |
| Total PAH[b] | 6 ($\mu g/m^3$) |
| Benzo[a]pyrene[b] | 0.4 ($\mu g/m^3$) |
| TWA Fume[b] | 700 ($\mu g/m^3$) |
| BIOLOGICAL | |
| Urine Samples | |
| Mutagenicity | Negative[c] |
| D-glucaric acid | Negative[c] |
| Thioethers | Negative |

[a] Ames test
[b] Mean values
[c] Smoking increased this parameter.

Table 3.15
Polynuclear Aromatic Hydrocarbon Contents in Asphalt Cements Separated from Asphalt Hot-Mixes (from Table 1 in Monarco et al., 1987).

| PAH | Concentration (µg/g) | | |
|---|---|---|---|
| | Sample 1 | Sample 2 | Sample 3 |
| Naphthalene | 28.7 | — | — |
| Acenaphthylene[b] | — | — | — |
| Acenaphthene[b] | 2.1 | 3.4 | 3.7 |
| Fluorene[b] | — | 1.0 | 1.2 |
| Phenanthrene[b] | 5.5 | 14.3 | 11.2 |
| Anthracene | 3.1 | — | 7.3 |
| Fluoranthene[b] | 24.3 | 31.0 | 40.0 |
| Pyrene[b] | — | 10.9 | 8.3 |
| Benzo[a]anthracene[a, b] | 10.1 | — | 5.0 |
| Chrysene[a, b] | 50.6 | 35.0 | 72.0 |
| Benzo[b]fluoranthene[a, b] | — | 29.0 | 36.3 |
| Benzo[k]fluoranthene[b] | 3.4 | 9.1 | 8.4 |
| Benzo[a]pyrene[a, b] | 2.1 | 13.1 | 7.1 |
| Benzo[ghi]perylene[b] | 2.7 | 4.5 | 1.9 |
| Dibenzo [a,h]anthracene[a, b] | 3.2 | 5.4 | 8.6 |
| Indeno[1,2,3-cd]pyrene[a, b] | 1.4 | 2.1 | 7.1 |
| Total PAH | 137.2 | 158.8 | 218.1 |

— not detected
[a] Carcinogenic hydrocarbon
[b] Mutagenic hydrocarbon

Table 3.16
Mutagenic Properties of DMSO Extracts of Asphalt Samples from Asphalt Hot-Mixes (from Table 2 in Monarco et al., 1987).

| Sample No. | DMSO Extract Residue (mg/plate) | Corresponding Dose of Bitumen (mg/plate) | Revertants/plate[a] | | | |
|---|---|---|---|---|---|---|
| | | | TA 98 Strain | | TA 100 Strain | |
| | | | -S9 | +S9 | -S9 | +S9 |
| 1 | 0.1 | 1.3 | 23±2 | 44±5 | 106±15 | 143±19 |
| | 5.0 | 65.2 | 34±5 | 62±9 | 165±24 | 207±31 |
| 2 | 0.1 | 1.1 | 22±3 | 36±4 | 127±16 | 138±18 |
| | 5.0 | 56.3 | 35±4 | 45±6 | 110±18 | 182±15 |
| 3 | 0.1 | 1.0 | 18±3 | 61±11 | 134±26 | 206±22 |
| | 5.0 | 43.3 | 37±4 | 50±7 | 145±18 | 167±19 |
| Negative Control (DMSO) | | | 19±4 | 33±8 | 120±10 | 150±20 |
| Positive Control[b] | | | 572±41 | 261±31 | 1358±91 | 896±78 |

[a] The results refer to the lowest and highest doses tested and are mean values (±SD) from two experiments (each dose level adonol tested in triplicate).
[b] TA98 - S: 2-nitrofluorene (1μg); TA98 + S9: Benzo[a]pyrene (1μg): TA100 - S9: sodium azide (1μg); TA100 + S9: Benzo[a]pyrene (1μg).

Table 3.17
Polynuclear Aromatic Hydrocarbons in Airborne Particulates Collected During Asphalt Hot-Mix Paving Operations (from Table 3 in Monarco et al., 1987).

| PAH | Concentration ($\mu g/m^3$)[c] $S_1$[d] | $S_2$[e] |
|---|---|---|
| Naphthalene | 0.18 | 0.24 |
| Acenaphthylene[b] | — | — |
| Acenaphthene[b] | 0.16 | 1.26 |
| Fluorene[b] | 0.02 | 0.08 |
| Phenanthrene[b] | 0.06 | 0.22 |
| Anthracene | 0.03 | 0.13 |
| Fluoranthene[b] | 0.39 | 1.13 |
| Pyrene[b] | 0.35 | 0.54 |
| Benzo[a]anthracene[a, b] | 0.54 | 3.50 |
| Chrysene[a, b] | 0.16 | 0.20 |
| Benzo[b]fluoranthene[a, b] | — | 1.03 |
| Benzo[k]fluoranthene[b] | 0.09 | 0.67 |
| Benzo[a]pyrene[a, b] | 0.03 | 0.61 |
| Benzo[g,h,i]perylene[b] | 0.01 | 0.19 |
| Dibenzo [a,h]anthracene[a, b] | 0.03 | 0.98 |
| Indeno[1,2,3-cd]pyrene[a, b] | 0.02 | 0.05 |
| Total PAH | 2.10 | 9.70 |

[a] Carcinogenic Hydrocarbon
[b] Mutagenic Hydrocarbon
[c] Mean values of two samplings.
[d] Samplings carried out for 2h consecutively with high-volume samplers.
[e] Samplings carried out for 2h, only during bitumen exposure, with high-volume samplers.

Table 3.18
Mutagenic Properties of Asphalt Fumes Collected During Hot-Mix Paving Operations (from Table 4 in Monarco et al., 1987).

| Extracts | Extract Residue (mg/plate) | Corresponding Dose of Airborne Particulate (mg/plate) | Revertants/plates TA98 Strain -S9 | +S9 | TA100 Strain -S9 | +S9 |
|---|---|---|---|---|---|---|
| Ethyl Ether Extracts | | | | | | |
| $S_1$ | 0.1 | 0.2 | 23±2 | 29±4 | 119±14 | 148±20 |
| | 6.0 | 12.5 | 15±3 | 55±10 | 120±30 | 138±17 |
| $S_2$ | 0.1 | 0.2 | 20±4 | 31±12 | 112±15 | 135±7 |
| | 6.0 | 12.3 | 31±6 | 36±4 | 131±12 | 129±11 |
| Acetone Extracts | | | | | | |
| $S_1$ | 0.05 | 5.0 | 19±6 | 25±2 | 105±19 | 137±22 |
| | 0.2 | 20.0 | 15±7 | 23±7 | 110±13 | 122±9 |
| $S_2$ | 0.05 | 15.0 | 17±4 | 24±3 | 97±10 | 119±24 |
| | 0.2 | 60.0 | 16±2 | 22±6 | 104±12 | 140±23 |
| Negative Control (DMSO) | | | 16±3 | 28±4 | 109±15 | 138±19 |
| Positive Control | | | 531±82 | 280±44 | 1402±127 | 820±91 |

[a] The results refer to the lowest and highest doses tested and are mean values (±SD) from two experiments (each dose and control was tested in triplicate).
[b]TA98 - S: 2-nitrofluorene (1μg); TA98 + S9: Benzo[a]pyrene (1μg): TA100 - S9: sodium azide (1μg); TA100 + S9: Benzo[a]pyrene (1μg) .

Table 3.19
Urinary Excretion of Mutagens by Subjects Exposed to Asphalt Fumes During Paving Operations and by Controls, According to Smoking Habits (from Table 1 in Pasquini et al., 1989a).

| Urine Mutagenicity | Smokers Exposure to Bitumen | | Non-Smokers[a] Exposure to Bitumen | |
|---|---|---|---|---|
| | Yes | No | Yes | No |
| Yes | 6 (100%) | 9 (100%) | 9 (82%) | 5 (28%) |
| No | 0 | 0 | 2 | 13 |
| Total | 6 | 9 | 11 | 18 |

[a]Significance of increase in urine mutagenicity with bitumen exposure was P<0.025 (based corrected Chi-square value).

Table 3.20

Mean Values of Mutagenic Activity in Urine of Subjects Exposed to Asphalt Fumes During Paving Operations and of Control Subjects (TA98 Strain + S9 mix)[a] (from Table 2 in Pasquini et al., 1989a).

| Groups | | Induced rev/100 ml urine (median values) | | | Induced rev/mmol creatinine (median values) | | |
|---|---|---|---|---|---|---|---|
| | | Morning | All Day | Significance[b] | Morning | All Day | Significance[b] |
| Total exposed (n=17) | | 74 | 157 | $P<0.05$ | 68 | 146 | N.S. |
| Total unexposed (n=27) | | 68 | 76 | | 74 | 89 | |
| Non-smokers | Exposed (n=11) | 57 | 139[c] | $P<0.001$ | 60 | 146[c] | $P<0.01$ |
| | Unexposed(n=18) | 58 | 60[d] | | 62 | 76[d] | |
| Smokers | Exposed (n=6) | 78 | 165[c] | N.S. | 76 | 174[c] | N.S. |
| | Unexposed (n=9) | 90 | 164[d] | | 88 | 221[d] | |

[a] Mean Values (± SD) of background and positive control (benzo[a]pyrene 1 μg/plate) mutatuin rates were 24 ± 6 and 215 ± 20 revertants/plate respectively.

[b] Statistical comparisons were carried out for all-day values by the Kruskal-Wallis Test.

[c] The differences between the values for exposed smokers and non-smokers were statistically not significant

[d] Statistical differences between unexposed smokers and non-smokers were: $P<0.005$ for rev/100 ml urine values and $P<0.001$ for rev/creatinine values.

N.S. = not significant

Table 3.21
Mean Values (± SD) of Thioethers/Creatinine Ratio (THIO/CR) in Urine Samples of Subjects Exposed to Asphalt Fumes During Paving Operations and Control Subjects, According to Smoking Habits (from Table 3 in Pasquini et al., 1989a).

| Groups | THIO/CR (mmol/mol) | | Significance[a] |
|---|---|---|---|
| | Morning | All Day | |
| Total Exposed | 6.93±3.42 | 8.71±3.18 | N.S. |
| Total unexposed | 6.96±3.41 | 6.63±3.46 | |
| Exposed | | | |
| Smokers | 7.68±4.76 | 10.58±3.44 | N.S. |
| Non-smokers | 6.55±2.67 | 7.70±2.66 | |
| Unexposed | | | |
| Smokers | 6.87±4.23 | 7.72±4.73 | N.S. |
| Non-smokers | 7.00±3.04 | 6.06±2.54 | |

[a] One-tailed F-test
N.S. = not significant

Table 3.22
Mean Values (± SD) of D-glucaric/Creatinine Ratio (GLA/CR) in Urine Samples of Subjects Exposed to Asphalt Fumes During Paving Operations and Control Subjects, According to Smoking Habits (from Table 4 in Pasquini et al., 1989a).

| Groups | GLA/CR (mmol/mol) Morning | GLA/CR (mmol/mol) All Day | Significance |
|---|---|---|---|
| Total Exposed | 3.62±1.20 | 3.83±1.41 | N.S. |
| Total unexposed | 3.45±3.38 | 3.64±1.45 | |
| Exposed | | | |
| Smokers | 3.14±1.03 | 4.14±0.92 | N.S. |
| Non-smokers | 3.63±1.40 | 3.66±1.10 | |
| Unexposed | | | |
| Smokers | 3.09±1.10 | 4.10±0.91 | N.S. |
| Non-smokers | 3.65±1.12 | 3.61±1.46 | |

[a]One-tailed F-test
N.S. = not significant

Table 3.23
Urinary Thioether Excretion Among Workers Exposed to Asphalt Fumes During Hot-Mix Preparation and Road Paving Operations (from Table 1 in Burgaz et al., 1988).

| Groups[a] | Thioether Excretion (mmol SH-/mol creatinine) | Significance[b] |
|---|---|---|
| Total Exposed (A) (n=12) | 6.34±1.27 | |
| Total Nonexposed (C) (n=37) | 5.09±0.43 | P>0.05 |
| Total Exposed (B) (n=32) | 6.75±0.78 | P>0.05 |
| Smokers | | |
| Exposed (A) (n=4) | 10.62±1.75 | |
| Nonexposed (C) (n=23) | 5.91±0.58 | P<0.05 |
| Exposed (B) (n=15) | 9.41±1.20 | P<0.05 |
| Nonsomokers | | |
| Exposed (A) (n=8) | 4.20±1.10 | |
| Nonexposed (C) (n=14) | 3.76±0.44 | P>0.05 |
| Exposed (B) (n=17) | 4.39±0.59 | P>0.05 |

[a] Group A consists of the workers in asphalt hot-mix preparation;
Group B consists of the workers in road paving koperations;
Group C consists of male office clarks not exposed to asphalt emissions.
[b] Statistical analyses were carried out by the one-tailed Student's *t*-test, $P<0.05$ indicates a statistically significant difference.

Table 4.1
Medical Assessments of Petroleum Refinery Workers
(adapted from text in Baylor and Weaver, 1968).

| Health Problems | Asphalt Workers | | Control Workers | |
|---|---|---|---|---|
| | Number | % | Number | % |
| Medical Histories | 360 | 100 | 277 | 100 |
| Cancer -lung | 0 | 0 | 1 | 0.36 |
| -colon | 0 | 0 | 1 | 0.36 |
| -stomach | 1 | 0.28 | 0 | 0 |
| -skin | 2 | 0.56 | 4 | 1.4 |
| Misc. lung disease | 31 | 8.6 | 12 | 4.3 |
| Misc. skin disease | 37 | 10.3 | 47 | 17.0 |
| Overweight | 111 | 30.8 | 88 | 31.8 |
| Physical Examinations | 462 | 100 | 379 | 100 |
| Skin cancer | 4‡ | 0.87 | 0 | 0 |
| Misc. lung disease | 40 | 8.6 | 24 | 6.3 |
| Misc. skin disease | 26 | 5.6 | 20 | 5.3 |
| Hypertension | 27 | 5.8 | 27 | 7.1 |
| Peptic ulcer | 12 | 2.6 | 8 | 2.1 |
| Heart disease | 17 | 3.7 | 14 | 3.7 |
| Excessive smoking*† | 121 | 26.2 | 89 | 23.5 |

* ≥ 20 cigarettes/day for ≥ 20 years
† Numbers are below actuality because the smoking question was eliminated from some of the questionnaires.
‡ Two workers had skin cancer prior to beginning work in asphalt operations.

Table 4.2
Typical Hazardous Materials and Exposures in Highway Construction and Maintenance Operations (from Table 1 in Maizlish et al., 1988).

| Hazard | Operations | Known and Suspected Health Effects |
|---|---|---|
| Asbestos | Brake and clutch repair | Asbestosis, lung cancer, mesothelioma |
| Asphalt | Paving, crack and joint filling, surface sealing, PCC base repair | Burns, dermatitis, photosensitization, lung cancer |
| Biological agents | Landscaping, roadside clean-up | Dermatitis, infectious disease, enteric illness, animal/insect bites, Rhus, sp. |
| Carbon monoxide | Toll booths/heavy equipment | Carboxyhemoglobin hypoxia |
| Coal tar | Surface scaling | Cancers at various sites |
| Diesel exhaust | Heavy equipment/toll booths | Lung cancer and cancers at other sites |
| Dusts | Power sweeping, abrasive blasting, chipping, pavement grinding | Respiratory irritation, silica exposure |
| Electrical hazards (PCB) | Installation of lighting | Electrocution, lymphopoietic cancers |
| Hydrogen sulfide | Asphalt patching | Respiratory irritation |
| Lead | Toll booth traffic | Neurobehavioral effects |
| Moving motor vehicle traffic | Traffic control, construction zone work | Trauma |
| Noise | Heavy equipment | Hearing loss |
| Pesticides | Weed control, plant disease and pest management, inhibitor spraying, highway spill clean up | Lymphopoietic cancers desmatisits |
| Portland cement | Paving, bridge repair | Dermatitis, stomach cancer |
| Solvents (toluene, xylene, TCE, TCA, kerosene, benzene, naphtha, gasoline) | Materials testing, striping, highway spills, bridge painting, sign maintenance, vehicle repair, degreasing, concrete curing | CNS depression, leukemia (benzene), dermatitis |
| UV/solar radiation | Sun/outdoor work | Skin cancer, melanoma (?), heat stroke |
| Welding fumes | Fence repair, bridge maintenance, guardrail and median barrier repair, vehicle and sign maintenance | Lung cancer |

Table 4.3
Standardized Proportional Mortality Ratios in CalTRANS White Males, 1970-1983, Highway Maintenance Classification at Separation (adapted from Table VI in Maizlish et al., 1988).

| Cause of Death | Observed | PMR | 95% Confidence Interval[a] |
|---|---|---|---|
| Total deaths | 307 | | |
| All malignant neoplasms | 81 | 117 | 93-146 |
| Cancer of the digestive organs | 25 | 151 | 97-223 |
| Cancer of stomach | 6 | 227 | 83-495 |
| All cancer of lung | 25 | 98 | 63-145 |
| Cancer of skin | 2 | 122 | 12-439 |
| Cancer of prostate | 7 | 226 | 91-466 |
| Cancer of brain and other CNS | 4 | 160 | 40-410 |
| All lymphopoietic cancer | 8 | 115 | 50-226 |
| Benign neoplasms | 3 | 345 | 69-1011 |
| All circulatory diseases | 110 | 83[b] | 68-99 |
| All respiratory diseases | 15 | 93 | 52-153 |
| Emphysema | 8 | 250[b] | 108-492 |
| All diseases of the digestive system | 15 | 92 | 51-152 |
| Cirrhosis of liver | 13 | 127 | 68-217 |
| All external causes | 73 | 145[c] | 114-182 |
| All accidents | 53 | 169[c] | 127-222 |
| Motor vehicle accidents | 33 | 196[c] | 134-276 |
| Suicides | 16 | 139 | 79-226 |

[a] Poisson coefficient intervals.
[b] $p < .05$, Poisson two-tailed test.
[c] $p < .01$.

Table 4.4
Description of the Minnesota Highway Maintenance Worker Cohort (from Table I in Parker et al., 1989).

| Subgroup | No. of Wokers | Mean Years Worked (SE)[a] | Mean Age Beginning Work (SE) | Mean Age Ending Work (SE) | Mean Year Starting Work |
|---|---|---|---|---|---|
| All workers | 4,849 | 13.9 (.15) | 35.3 (.17) | 49.9 (.21) | 1957 |
| Urban workers | 1,508 | 11.3 (.22) | 34.7 (.32) | 46.5 (.38) | 1963 |
| Rural workers | 3,341 | 15.1 (.19) | 35.5 (.20) | 51.5 (.24) | 1955 |

[a] SE = standard error.

Table 4.5
Standardized Mortality Ratios for Selected Cancer Mortality Among the Minnesota Highway Maintenance Worker Cohort, 1945-1984 (adapted from Table I in Bender et al., 1989).

| Cancer of Death (ICD-9)[a] | Observed | Expected | SMR | 95% Confidence Interval |
|---|---|---|---|---|
| All causes (001-999) | 1,530 | 1,676.0 | 91[b] | 86-96 |
| All cancer (140.0-208.9) | 274 | 328.8 | 83 | 73-94 |
| Mouth, pharynx (140.0-149.9) | 7 | 8.0 | 88 | 35-181 |
| All gastrointestinal (150.0-159.8) | 90 | 109.2 | 82 | 66-101 |
| Stomach (151.0-151.9) | 23 | 25.2 | 91 | 58-137 |
| Intestines (152.0-153.9) | 30 | 34.9 | 86 | 58-123 |
| Rectum (154.0-154.8) | 8 | 12.1 | 66 | 28-130 |
| Pancreas (157.0-157.9) | 17 | 19.2 | 89 | 52-142 |
| All respiratory (160.0-165.9) | 57 | 82.6 | 69 | 52-90 |
| Trachea, bronchus, lung (162.0-162.8) | 54 | 77.9 | 69 | 52-90 |
| Male genital (185.0-187.9) | 41 | 39.5 | 104 | 75-141 |
| Prostate (185.0-185.9) | 39 | 38.1 | 100 | 71-137 |
| Testes (186.0-186.9) | 2 | 0.9 | 217 | 26-783 |
| Urinary organs (188.0-189.9) | 19 | 20.7 | 92 | 55-144 |
| Kidney (189.0-189.2) | 6 | 9.6 | 63 | 23-137 |
| Bladder (188.0-188.9) | 12 | 11.0 | 109 | 56-190 |
| Lymphoreticular (200.0-208.9) | 34 | 35.7 | 95 | 66-133 |
| Lymphosarcoma (200.0-200.8) | 7 | 6.2 | 113 | 45-233 |
| Hodgkin's disease (201.0-201.9) | 2 | 3.4 | 58 | 7-209 |
| Leukemia (204.0-208.9) | 17 | 15.9 | 107 | 62-171 |
| Multiple myeloma (203.0-203.1) | 3 | 5.7 | 53 | 11-155 |
| Other lymphoreticular (202.0-202.9) | 5 | 4.5 | 110 | 36-257 |
| Other | | | | |
| Melanoma (172.0-172.9) | 0 | 2.9 | 0 | — |
| CNS (191.0-192.9) | 6 | 9.2 | 66 | 24-144 |

[a]International Classification of Diseases, 9th revision equivalents.
[b]$p<.01$.

Table 4.6

Standardized Mortality Ratios for Noncancer Mortality Among the Minnesota Highway Maintenance Worker Cohort, 1945-1984 (adapted from text and Table II in Parker et al., 1989).

| Cause of Death (ICD-9)[a] | Observed | Expected | SMR | 95% Confidence Interval |
|---|---|---|---|---|
| All causes (001-999) | 1,530 | 1,676.0 | 91[c] | 86-96 |
| All infective and parasitic(001-139) | 11 | 14.7 | 75[c] | 38-134 |
| Nutritional, metabolic and immune diseases (240-279) | 39 | 32.8 | 119 | 85-163 |
| Hematopoietic disorders (280-289) | 4 | 4.0 | 100 | 27-256 |
| Psychiatric disorders, alcoholism (290-319) | 4 | 4.2 | 96 | 26-246 |
| Neurologic diseases (320-389) | 14 | 17.3 | 81 | 44-136 |
| All circulatory (390-459) | 865 | 950.5 | 91[d] | 85-97 |
| All heart disease | 677 | 727.0 | 93 | 86-100 |
| Ischemic heart | 601 | 627.9 | 96 | 88-104 |
| Cerebrovascular | 130 | 162.5 | 80[c] | 66-95 |
| Arteriosclerosis | 16 | 19.0 | 74 | 35-136 |
| All respiratory (460-519) | 105 | 102.9 | 102 | 83-123 |
| Chronic and unspecified bronchitis | 7 | 4.8 | 147 | 59-303 |
| Emphysema | 19 | 20.2 | 94 | 57-147 |
| Diseases of the digestive system (520-579) | 53 | 63.8 | 85 | 64-111 |
| Cirrhosis of liver | 19 | 24.0 | 79 | 48-123 |
| Diseases of genito-urinary system (580-629) | 17 | 22.1 | 77 | 45-123 |
| Diseases of skin (680-709) | 0 | | 0 | |
| Bone and connective tissue diseases (710-739) | 5 | 3.3 | 153 | 50-357 |
| Senility and ill-defined conditions (780-799) | 13 | 13.1 | 99 | 53-169 |
| All E codes (800-999) | 116 | 110.5 | 105 | 87-126 |
| Other injuries[b] | 44 | 44 | 100 | 73-134 |
| Transportation injuries (E800-E848, E929.0, E939.1) | 53 | 38.4 | 138[c] | 103-180 |
| Residual and undefined | 1 | 0.8 | 119 | 3.0-661 |

[a] International Classification of Disease, 9th revision equivalents.
[b] Does not include suicide and homicide.
[c] $p < 0.01$.
[d] $p < 0.05$.

Table 4.7

Tumor Production in Mice from Dermal Application of Asphalt (adapted from Table II in Simmers, 1965a).

| Asphalt | No. Animals to Start | No. Animals Coming to Autopsy | No. Histologic Examinations | Cancers Found | Percent Cancers in Autopsied Animals | Other Findings |
|---|---|---|---|---|---|---|
| Air-Refined | 25 M - 25 F | 10 | 10 | 0 | 0 | 1 adenoma of lung |
| Steam-Refined | 33 M - 30 F | 21 | 12 | 3 | 14 | 1 papilloma |
| (Start- | 25 M - 25 F) | | | | | 2 papillomas, |
| *(Added- | 8 M - 5 F) | | | | | 1 adenoma of lung |
| Air-Refined diluted with Toluene | 10 M -10 F | 20 | 12 | 9 | 45 | 2 adenomas of lung, chronic dermatiitis |
| Toluene Controls | 5 M -10 F | 8 | 6 | 0 | 0 | 1 papilloma, chronic dermatitis |

*15 M and 12 F survived an epidemic of pneumonitis.

Table 4.8

Tumor Production in Mice from Dermal Application of the Combined Saturate and Aromatic Fractions of Steam-Refined Asphalt (from Table II in Simmers, 1965b).

| No. Animals Studies Microscopically | % of the 40 Animals Autopsied | % of the 30 Animals Studied Microscopically | Pathology |
|---|---|---|---|
| 4 | 10 | 13 | Epilation, Hyperkeratosis, Lengthened rete pegs, epidermal atypia, chronic dermatitis. |
| 13 | 33.3 | 43 | Papillomas; one had and underlying rhabdomyosarcoma. |
| 7 | 15 | 20 | Epidermoid cancers; one animal with an epidermoid cancer of the anus also had a leiomyosarcoma of the small intestine. |
| 5 | 15 | 20 | Squamous cell cancer; 1 metastatic to lung. |
| 1 | 2.5 | 3.3 | Cancer of skin accessory structures (sebaceous gland). |
| 10 | 25 | | Not subjected to microscopic examination because of minimal reaction – slight epilation and scaly skin. |
| 13 | 32.5 | 43.3 | Total Cancers |

Table 4.9

Neoplastic Reactions in Animals Receiving Cutaneous Applications of Road Asphalts* (adapted from text and Table 1 in Hueper and payne, 1960).

| Source of Asphalt | Species | No. | Skin Carcinoma | Skin Papilloma | Thigh Sarcoma | Leukemia Lymphoma | Lymph Node | Liver Sarcoma | Uterus Carcinoma |
|---|---|---|---|---|---|---|---|---|---|
| Venezuela | Mouse | 50 | 0 | 0 | 1 | 1 | 0 | 0 | 0 |
| | Rabbit | 30 | 0 | 0 | 2 | 0 | 2 | 0 | 0 |
| Mississippi | Mouse | 50 | 0 | 0 | 1 | 1 | 0 | 0 | 0 |
| | Rat | 30 | 0 | 0 | 1 | 0 | 3 | 3 | 1 |
| Oklahoma | Mouse | 50 | 0 | 0 | 0 | 0 | 1 | 0 | 0 |
| | Rat | 30 | 0 | 0 | 4 | 0 | 0 | 0 | 1 |
| California | Mouse | 50 | 1 | 0 | 1 | 0 | 1 | 0 | 0 |
| | Rat | 30 | 0 | 0 | 6 | 0 | 4 | 1 | 1 |
| Control | Mouse[a] | 144 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | Mouse[b] | 200 | 0 | 0 | 0 | 1 | 0 | 0 | 0 |
| | Rat | 60 | 0 | 0 | 0 | 0 | 4 | 1 | 3 |

* Diluted with tricaprylin in 1:1 ratio.
[a] Subcutaneous injection of tricaprylin alone.
[b] Colony animals administered no control substances.

Table 4.10
Tumor Production in Mice by Dermal Application of Atmospheric Distillation Residues from Russian Crude Oils (adapted from text in Kireeva, 1968).

| Material[a] | No. Animals | | Skin Tumor | Lung Tumor |
|---|---|---|---|---|
| | Start | Surviving 9 months | | |
| A | 50 | 43 | 2 | 5 |
| B | 40 | 30 | 0 | 1 |
| C | 50 | 43 | 2 | 1 |
| D | 37 | 30 | 0 | 1 |
| Control[b] | 23 | 23 | 0 | 1[c] |

[a] Residues in solution with 40% benzene.
[b] Benzene only.
[c] Several adenomas formed in one animal.

Table 4.11
Tumor Production in Mice from Dermal Application of Asphalts of Known PAH Content (adapted from Table 2 in Wallcave et al., 1971).

| Group | | No. of Animals Autopsied | No. of Tumor-Bearing Animals | Skin Tumors | |
|---|---|---|---|---|---|
| | | | | Carcinomas | Papillomatous Growths |
| Asphalt | A | 24 | 0 | 0 | 0 |
| | B | 25 | 1 | 0 | 1 |
| | C | 28 | 0 | 0 | 0 |
| | D | 32 | 0 | 0 | 0 |
| | E | 27 | 1 | 1 | 0 |
| | F | 27 | 2 | 0 | 2 |
| | G | 28 | 2 | 0 | 2 |
| | H | 27 | 0 | 0 | 0 |
| | Total | 218 | 6 | 1 | 5 |
| Control | | 26 | 1 | 0 | 1 |

Table 4.12

Tumor Production in Mice by Dermal Application of Cold Lake Bitumen (adapted from Table 4 in McKee and Lewis, 1987).

| Test Material | Mean Survival (weeks) | Tumor Response[a] | | Median Latency[b] (weeks) |
|---|---|---|---|---|
| | | Malignant | Benign | |
| Crude Bitumen[c] | 88[d] | 8 | 5 | 106 (97-116)[e f] |
| White Oil (Negative Control) | 86 | 0 | 0 | ND |
| Toluene (Vehicle Control) | 83 | 0 | 0 | ND |

ND, not determined

[a] Animals were classified on the basis of the most advanced tumor type in the treatment area. The number shown is the total number of mice in each category from a test group of 50 animals.

[b] The brackets define the 95% confidence interval around the median latency as estimated by the Weibull method.

[c] The crude bitumen was applied as a 75% suspension in toluene.

[d] Mean survival was estimated by the product limit method.

[e] Tumor yield is significantly different from the negative control.

[f] Median latency is significantly different from the negative control.

Table 4.13

Other Primary Tumors in Mice Treated with Cold Lake Bitumen (adapted from Table 5 in McKee and Lewis, 1987).

| Tumor Type | Crude Bitumen | White Oil (Negative Control) | Toluene (Vehicle Control) |
|---|---|---|---|
| Alveolar-bronchiolar carcinoma | 1[a] | 0 | 0 |
| Lymphoma | 1 | 1 | 0 |
| Granulocytic leukemia | 3 | 0 | 1 |
| Histiocytic sarcoma | 0 | 0 | 0 |
| Reticulum cell sarcoma | 1 | 0 | 1 |
| Hemangioma—hemongio-sarcoma | 1 | 4 | 0 |
| Hemangioendothelioma | 1 | 0 | 1 |
| Hepatocellular carcinoma | 13 | 12 | 14 |
| Bile duct carcinoma | 0 | 0 | 0 |
| Basal cell carcinoma | 0 | 0 | 0 |
| Fibrosarcoma | 0 | 0 | 0 |
| Squamous cell carcinoma (skin) | 0 | 0 | 0 |
| Squamous cell carcinoma (stomach) | 0 | 0 | 0 |
| Fibrous histiocytoma | 1[b] | 0 | 0 |

[a] All mice with tumors were counted from a test group of 50 animals with each type of tumor.
[b] This tumor arose in skin outside the treatment area.

Table 4.14
Tumor Production in Mice from Subcutaneous Injection of Undiluted Asphalt (adapted from Table II in Simmers, 1965a).

| Asphalt | No. of Animals to Start | No. of Animals Coming to Autopsy | No. of Histologic Examinations | Cancers Found | % Cancers in Autopsied Animals | Other Findings |
|---|---|---|---|---|---|---|
| Steam-Refined | 25 M -25 F | 32 | 15 | 0 | 0% | 1 adenoma of lung |
| Air-Refined | 25 M -25 F | 38 | 24 | 5 | 13% | 5 aderomas of lung |

Table 5.1
Estimated Yearly PAH Emissions to the Atmosphere in Three Industrialized Countries (from Table 9 in Bjørseth and Ramdahl, 1985).*

| Source | Norway Metric tons/year | Norway Percent | Sweden Metric tons/year | Sweden Percent | U.S.A. Metric tons/year | U.S.A. Percent |
|---|---|---|---|---|---|---|
| Residential combustion | | | | | | |
| Wood, coal | 48 | 16 | 96 | 38 | 700 | 12 |
| Oil, gas | 14.5 | 5 | 36 | 14 | 15 | 0.3 |
| Industrial production | | | | | | |
| Coke manufactoring | 5.1 | 2 | 18 | 7 | 630 | 11 |
| Carbon black | | | <0.1 | <0.1 | 3 | <0.1 |
| Asphalt production | 0.1 | <0.1 | 0.3 | <0.1 | 4 | <0.1 |
| Aluminum production | 160 | 54 | 35 | 14 | 1000 | 17 |
| Iron and steel works | 34 | 12 | | | | |
| Ferroalloy industry | 3.5 | 1 | 1 | 0.4 | | |
| Petroleum cracking | | | <0.1 | <0.1 | | |
| Power generation | | | | | | |
| Coal and oil-fired power plants | | | <0.1 | <0.1 | 1 | <0.1 |
| Peat, wood straw | 0.1 | <0.1 | 6.5 | 3 | | |
| Industrial boilers | 0.2 | 0.4 | 6.5 | 3 | 400 | 7 |
| Incineration | | | | | | |
| Municipal incineration | 0.3 | <0.1 | 2.2 | 0.9 | 50 | 0.8 |
| Open burning | 0.4 | <0.1 | | | 100 | 2 |
| Forest fires | 7 | 2 | 1.3 | 0.5 | 1000 | 17 |
| Agricultural burning | 6 | 2 | | | | |
| Mobile sources | | | | | | |
| Gasoline automobiles | 13 | 4 | 33 | 13 | 2100† | 35 |
| Diesel automobiles | 7 | 2 | 14 | 6 | 70 | 1 |
| Air Traffic | 0.1 | <0.1 | <0.1 | <0.1 | | |
| Total | 295 | | 250 | | 6000 | |

* Numbers are encumbered with great uncertainties. To be used as an indicator of order of magnitude.
† Approximately 50% of U.S. cars have catalytic converters. This value does not represent a correction for using catalytic converters.

Table 5.2
Simulated Rainfall Leachability from Hot-Mix Pavement (adapted from Table II in Nielson et al., 1969).

| Time from Application | Asphaltic Material Removed (g/sq.ft.) | Asphaltic Material Removed (lb/mile) |
|---|---|---|
| 2 hr | 0.0035 | 0.8 |
| 5 hr | 0.0043 | 1.0 |
| 1 day | 0.0013 | 0.3 |
| 2 day | 0.0016 | 0.4 |
| 5 day | 0.0010 | 0.2 |
| 12 day | 0.0010 | 0.2 |

* Mile of roadway having 20 ft. (6.1-m) road bed.

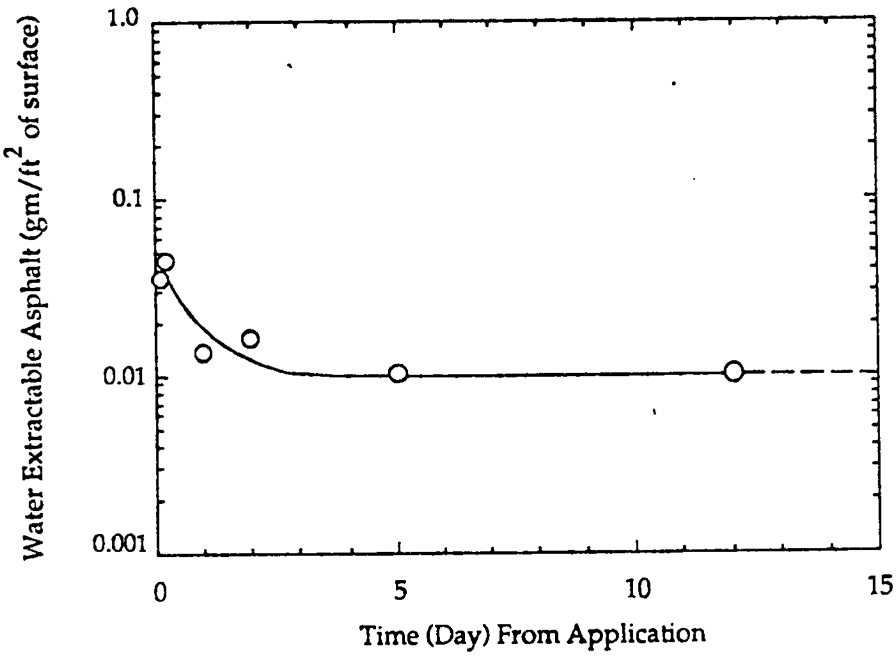


Figure 5.3 Area rainfall study: Comparison of areal leaching from hot-mixasphalt surface (adapted from Table 2 in Nielson et al., 1969).

## TABLE 6.1—GUIDE FOR LOADING ASPHALT PRODUCTS (8)

| LAST PRODUCT IN TANK | PRODUCT TO BE LOADED | | | |
|---|---|---|---|---|
| | Asphalt Cement | Cutback Asphalt | Cationic Emulsion | Anionic Emulsion |
| Asphalt Cement | OK to load | OK to load | Empty to no Measurable Quantity | Empty to no Measurable Quantity |
| Cutback Asphalt | Empty* | OK to load | Empty to no Measurable Quantity | Empty to no Measurable Quantity |
| Cationic Emulsion | Empty* | Empty to no Measurable Quantity | OK to load | Empty to no Measurable Quantity |
| Anionic Emulsion | Empty* | Empty to no Measurable Quantity | Empty to no Measurable Quantity | OK to load |
| Crude Petroleum and residual fuel oils | Empty* | Empty to no Measurable Quantity | Empty to no Measurable Quantity | Empty to no Measurable Quantity |
| Any product not listed above | Tank must be cleaned | Tank must be cleaned | Tank must be cleaned | Tank must be cleaned |

*Any material remaining will produce dangerous conditions.

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