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HIGH PRODUCTION VOLUME (HPV) CHEMICAL CHALLENGE PROGRAM

**TEST PLAN
ASPHALT CATEGORY**

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by

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Table of Contents

Plain Language Summary	3
Description of Asphalt Category	5
Composition of Asphalts	8
Category Rationale	10
Evaluation of Existing Health Effects Data and Proposed Testing	10
Evaluation of Existing Physicochemical and Environmental Fate Data	15
Evaluation of Existing Ecotoxicity Data and Proposed Testing	19
Matrix of Available Adequate Data and Proposed Testing	21
References	22
Tables	
Table 1. Elemental Analysis of Asphalts from Different Crude Petroleum Sources	5
Table 2. Typical Physical/Chemical Properties of Asphaltic Materials	6
Table 3. Representative Ecotoxicity Data for Lubricating Base Oils and Aromatic Extracts	20
Table 4. Matrix of Available Data and Proposed Testing	21
Table A3-1. Grades and Characteristics of Roofing Asphalts	31
Table A4-1. Carcinogenicity of Asphalts	34
Appendices	
Appendix 1. Asphalt Category	28
Appendix 2. Asphalt Manufacturing	29
Appendix 3. Commercial Uses of Asphalt	31
Appendix 4. Asphalt Carcinogenicity Studies	33
Figures	
Figure A2-1. Main Processing Methods in the Manufacture of Asphalt	30

Plain Language Summary

This test plan focuses on asphaltic materials, i.e., heavy refinery streams such as asphalt, vacuum residuum and other compositionally similar residuum streams that are derived from the vacuum distillation of petroleum. These streams are sold as is, blended together, or subsequently processed (air blowing, solvent deasphalting, and for some residues, thermal conversion) to produce a variety of end use asphalt products that conform to specific product performance specifications.

Asphaltic materials are complex hydrocarbon mixtures with molecular weight ranging from 500-2000, high boiling ranges (400-550⁰C; 752-1021⁰F), and carbon numbers predominantly higher than C25. Because of their large molecular size, high viscosity, low solubility, and negligible vapor pressure, these refinery streams are not readily bio-available and demonstrate minimal toxicological activity. Heating of asphalts to facilitate paving and roofing applications produces fumes comprised of the lower molecular weight components of petroleum asphalt, which include low levels of some biologically active 3-7 ring polycyclic aromatic compounds (PAC), which may be inhaled or deposited on the skin or clothing. Generating conditions (temperature, degree of agitation, and duration of heating) significantly affect toxicological results.

The majority of toxicological information on materials in this category was developed on commercial end use asphalt products, rather than using individual refinery streams. Results in animal studies and human monitoring studies demonstrate that acute toxicity of asphalts and asphalt fumes is low and effects are transitory. Systemic toxicity of undiluted asphalt in repeat dermal exposure studies over long durations (90 days or longer) was limited to skin irritation but not skin cancer, although dilution in organic solvents produced some skin tumors depending on the solvent. Inhalation exposure to asphalt fumes for 90 days or longer induced irritation in nasal passages and the lung, and no other significant systemic toxicity or cancer. Mouse skin painting studies indicated that asphalt fumes generated under laboratory conditions of relatively high temperature and long duration [4-16.5+ hours] can produce mutations *in vitro* and skin tumors. Under field conditions of lower generating temperature and shorter duration, asphalt fumes were not active mutagens. Asphalt fumes did not act as tumor promoters or co-carcinogens. The presence and degree of mammalian toxicity is correlated with the presence and quantity of biologically active 3-7 ring PAC in asphalt and asphalt fumes. *In vitro* genetic toxicity studies demonstrated that whole asphalts are inactive or weakly mutagenic depending on the solvent employed. Fume condensates were mutagenic and severity of effect was correlated with the temperature under which the fumes were generated. Cytogenetic damage *in vivo* was not demonstrated in rats treated orally with vacuum residuum samples or in road pavement workers exposed to asphalt fumes in the workplace. However, when asphalt fume condensate was instilled intratracheally in rats, increased incidence of micronucleus formation was reported in bone marrow polychromatic erythrocytes at a cytotoxic high dose and DNA adducts were observed in lungs. No developmental or reproductive toxicity studies have been conducted on either asphalts, vacuum residuum or on fumes derived from these streams.

Substances in the asphalt HPV category are not expected to adversely impact the environment due to the physical and chemical properties of these materials. At ambient temperatures, asphaltic substances are semi-solid to solid with negligible vapor pressure. Upon release in the environment, such materials will tend to clump together and not disperse. Some hydrocarbon compounds have been measured in asphalt leachate water, but concentrations have been extremely low (part per trillion levels) and below any regulatory threshold levels. Because of their high molecular weights and hydrophobic characteristics, constituent hydrocarbons in asphalts have

extremely low water solubility and low bioavailability to aquatic organisms. Although bacteria may utilize hydrocarbon molecules as an energy source, biodegradation of asphalts by standard laboratory biodegradability tests is not expected to be measurable.

Asphaltic materials are not expected to show toxicity to aquatic organisms. Although no standard laboratory studies exist on asphalts, aquatic testing of similar petroleum products with lower molecular weights and higher water solubilities (i.e. lubricating base oils, aromatic extracts) have not demonstrated acute or chronic aquatic toxicity. Asphalt is currently used by the states of Washington and Oregon as liners on fish hatchery ponds for the propagation of millions of fish.

No additional environmental testing is proposed. However, an inhalation reproductive/developmental toxicity-screening test (OECD 421) in rats of an asphalt fume is proposed. Results of these studies combined with currently available results on asphalts, and compositionally similar heavy refinery streams are adequate to complete the hazard profile for streams in this category.

Description of Asphalt Category

Asphaltic materials, i.e., heavy refinery streams such as asphalt, vacuum residuum and other compositionally similar heavy residual streams, are derived from the vacuum distillation of petroleum. These streams are either sold as is, blended together, or subsequently processed (air blowing, solvent deasphalting, and for some residues, thermal conversion) to produce a variety of end use asphalt products that achieve specific product performance specifications.

The “end use product”, (Asphalt in the US or Bitumen in Europe) is defined as the residuum produced from the non-destructive distillation of crude petroleum at “atmospheric pressure and/or under reduced pressures in the presence or absence of steam” (Puzinauskas and Corbett, 1978). Asphalt also occurs as a natural deposit, the residue resulting from the evaporation and oxidation of liquid petroleum. Elemental analyses indicate that most asphalts contain 79-88 weight % (wt %) carbon, 7-13 wt% hydrogen, traces to 8 wt% sulfur, 2-8 wt% oxygen, and traces to 3 wt% nitrogen (Speight, 1992) and trace amounts of vanadium, nickel, aluminum and silicon. Distribution of components varies with the source of the crude oil [Table 1].

Table 1: Elemental analysis of asphalts from different crude petroleum sources

Crude Source	Carbon wt %	Hydrogen wt %	Nitrogen wt %	Sulfur wt %	Oxygen wt %	Vanadium ppm	Nickel ppm
Mexican blend	83.77	9.91	0.28	5.25	0.77	180	22
Arkansas-Louisiana	85.78	10.19	0.26	3.41	0.36	7	0.4
Boscan	82.90	10.45	0.78	5.43	0.29	1380	109
California	86.77	10.94	1.10	0.99	0.20	4	6

NIOSH, 2000, Speight, 1992

Asphalts are composed of mainly high molecular weight hydrocarbons, are black or dark-brown viscous liquids or solids at ambient temperature, are insoluble in water at 20°C, and are partially soluble in aliphatic organic solvents and fully soluble in carbon disulfide, chloroform, acetone or ether (Sax and Lewis, 1987). The members of this HPV category, listed in Appendix 1, all have high carbon to hydrogen ratios with carbon numbers predominantly greater than C25, boiling point ranges >400°C, high viscosity and negligible vapor pressure (Table 2).

In the US and Europe, 84% of asphalt is used in paving, and 15% in roofing. Only about 1% is used for other purposes such as waterproofing, damp proofing, insulation and paints (AI, 1990a). In the U.S., approximately 33 million tons of asphalt materials were produced in 2000 (AI, 2001). Modifying the refining processes can create different types of asphalts, ranging from sticky liquids to heavy brittle solids with variable industrial and chemical properties.

Table 2: Typical Physical/Chemical Properties of Asphaltic Materials

NA = Data not available

1-US EPA TSCA Chemical Inventory, 2003; 2- CONCAWE, 2003; 3- CONCAWE, 2001

4- Marathon Ashland Petroleum Asphalt and Oxidized Asphalt MSDS sheet, 1998.

5- Pennzoil 2600 Vis Resin MSDS sheet, 1998

CAS Number	Hydrocarbon Chain Length	Boiling Point	Softening Point	Vapor Pressure	Specific Gravity	Reference
Asphalt (Penetration) 8052-42-4	> C25	>470 ⁰ C	30-60 ⁰ C	Negligible	0.95-1.1	[1-4]
Asphalt (Hard) 8052-42-4	> C25	>550 ⁰ C	60-75 ⁰ C	Negligible	NA	[1, 2]
Vacuum Residues 64741-56-6	> C34	>495 ⁰ C	NA	Negligible	0.98-1.1	[1]
Raffinates, Residual oil Decarbonization 64742-07-0	> C34	>495 ⁰ C	NA	Negligible	NA	[1]
Petroleum Resins 64742-16-1	NA	>482 ⁰ C	NA	Negligible	0.94	[1, 5]
Residues, Hydro-desulfurized vacuum 64742-85-4	> C34	>495 ⁰ C	NA	Negligible	NA	[1]
Asphalt, Oxidized 64742-93-4	>C25	>400 ⁰ C	60-130 ⁰ C	Negligible	1.0-1.1	[1-4]

Asphalt Production

Asphalt streams are derived from the atmospheric and vacuum distillation of crude oil followed by subsequent processes (air blowing, solvent deasphalting, and for some residues, thermal conversion) to achieve the appropriate product characteristics. Each step in the refining process, beginning with the residuum from atmospheric distillation, is designed to extract the maximum high value distillates from the residue until only the high boiling, high molecular weight components remain to be marketed as commercial asphalt or as blending components of asphalts. With heavy crude oils, the vacuum residuum can often be a “commercial asphalt”. With lighter crude oils, these residues are feedstock for further processing. The steps in asphalt production are fully described in Appendix 2. This category does not include asphalt derivatives in which mixing with industrial process oils or heavy distillates (fluxed asphalts), additions of emulsifiers or elastomers alter the chemical composition of the product.

These streams and variations of them are typically used to produce the three main types of commercial asphalts (CONCAWE, 1992). Commercial uses and descriptive terms for asphalt products are found in Appendix 3.

1. Penetration Grade (asphalt cements, viscosity-grade asphalts) is produced from crude oil atmospheric distillation residues by further processing such as vacuum distillation (straight run asphalts), thermal conversion, partial oxidation (air rectification/semi-blowing) or solvent precipitation. A combination of these processes can be used to meet application specifications for road surfacing or in roofing applications.
2. Hard Asphalts (Hard Bitumens) are manufactured using similar processes to penetration grades but have lower penetration values and higher softening points. They are hard and more brittle, and are used primarily in the manufacture of asphalt paints and enamels.
3. Oxidized (Air blown) Asphalts are produced by passing air through hot, soft asphalt feedstock under controlled conditions, producing a higher softening point material with reduced susceptibility to changes in temperature and greater resistance to imposed stress. Applications include roofing materials, waterproof papers, electrical components, pipe coating, undersealing of concrete pavements, hydraulic applications, membrane envelopes, and the manufacture of paint.

Asphalts are not coal tar. Asphalts have been confused with coal tar and coal tar pitch, which can also be used for roofing and paving applications because both materials have a “tarry” consistency. Outside of the US (Europe), coal tar and coal tar pitch was used in road building before and during World War II due to a shortage of asphalt cement. However, some researchers have shown that coal tar materials have not been used in asphalt paving formulations after the 1970s (Kriech, et. al, 1997; Blackburn, et al., 1999). Coal tar and coal tar pitch are obtained as a byproduct of the destructive distillation of bituminous coal to produce coke by thermal cracking at high temperatures (458-1214⁰C; 850-2200⁰F). Coal tar contains highly condensed-ring aromatic compounds with a greater proportion of unsubstituted polycyclic aromatic compounds (PAC) in the toxicologically active 3-7 ring size range. In contrast, asphalts contain much larger proportions of high molecular weight paraffinic and naphthenic hydrocarbons and their derivatives that, because of their size, viscosity, and limited solubility are not readily bio-available and have minimal toxicological activity. Thus, measurements of routinely monitored polycyclic aromatic hydrocarbons (PAH) such as benzo(a)pyrene, are not indicators of potential carcinogenic activity of asphalts because they are present in extremely low concentrations and most asphalt PAC are alkylated. Fumes generated from asphalt are primarily aliphatic with a high proportion of saturates (60%, Brandt et al., 1985)

and demonstrate much less toxicological activity than coal tar fumes comprised almost entirely of aromatic compounds (>99%). Study results presented in this test plan do not include data for coal tar or asphalt containing coal tar.

COMPOSITION OF ASPHALTS

The chemistry of asphalt products is very complex because of the complex nature of the petroleum crude oils from which they are derived. The chemistry is also affected by the varying refining processes designed to meet specifications of performance rather than of a set chemical composition. Asphalts are comprised of asphaltenes, resins, aromatic and saturate components. Asphalts are regarded as colloidal systems (Witherspoon, 1962; Read and Whiteoak, 2003; Petroleum Handbook, 1987; IARC, 1985) consisting of asphaltene micelles dispersed in an oily matrix of components with lower molecular weight. The micelles are considered to be asphaltenes with an adsorbed sheath of aromatic resins of high molecular weight as a stabilizing solvating layer. Moving away from the center of the micelle, there is a gradual transition to less aromatic resins, and the layer extends outward into the less aromatic oily dispersion residuum.

The major chemical groups in produced asphalt are described as follows:

Asphaltenes: Brittle, brown-black amorphous solids, which are highly condensed aromatic compounds with molecular weight 500-1000 amu, constitute 5-25% of the weight of asphalts. They are comprised of one or two chromophores containing 4 to 10 fused rings each, with a significant number of alkyl substituents. A higher proportion of asphaltenes are present in the harder asphalts.

Resins: Brown-black, adhesive, shiny solids or semi-solids comprised of heterogeneous polar aromatic compounds with small amounts of oxygen, nitrogen, and sulfur with molecular weights of 800-2000, constitutes 15-25% of the weight of asphalts. They can be considered lower molecular weight asphaltenes and are dispersing agents for asphaltenes. The proportion of resin to asphaltenes governs to a degree the solidity or gel-type characteristic of the asphalt.

Aromatic oil components: Viscous dark brown liquids containing mainly carbon, hydrogen and sulfur with minor amounts of oxygen and nitrogen, with a molecular weight of 500-900, constitute 45-60% of the weight of the asphalt. They are compounds with aromatic and naphthenic-aromatic nuclei with side chain constituents.

Saturated oil components: Viscous liquids or solids ranging from straw to water-white color, consisting mainly of long chain saturated hydrocarbons with some branched chain compounds, alkyl aromatics with long side chains and cyclic paraffins (naphthenes), with a molecular wt of 500-1000, constitute 5-20% of the weight of the asphalt.

The proportions of the chemical groups vary in asphalts because of significant differences in petroleum crude oils that vary from field to field and even from different locations within the same field, as well as differences in refining processes.

Being derived from crude oil, asphalts contain polycyclic aromatic compounds (PAC), which include low levels of some biologically active 3-7 ring PAC, that may be inhaled or deposited on the skin or clothing. These PAC constituents are present in asphalts in lower concentrations than in the parent crude oil because the refining processes used to make asphalt in the United States remove

most species boiling below 538^oC (1000^oF). Additionally, these refining processes do not involve temperatures or other conditions that result in significant thermal cracking that would increase the presence of biologically active 3-7 ring PACs. The resulting content of known carcinogenic PACs in asphalts is in the low parts per million range (AI, 1990a). Biologically active PAC that may be present in residues from vacuum distillates are derived from incomplete separation in the distillation column, addition of lower viscosity distillates in the lubricant range prior to deasphalting [e.g. to increase production of residual lubricant oil], or lowering the vacuum residuum cut-point [below 1000^oF]. Otherwise, comparatively low manufacturing and use temperatures of asphalt do not facilitate formation of biologically active 3-7 ring PACs.

Although the total sulfur content of asphalts may vary considerably (trace to 8 wt %), the sulfur does not influence toxicity from exposure to asphalt or asphalt fume because the sulfur is largely entrained in the asphalt matrix and released slowly if at all. A significant amount of the sulfur is in the form of heterocyclic sulfur compounds with multiple fused rings and large molecular weights due to alkylation, resulting in minimal bioavailability. Some sulfur is released as H₂S and low molecular weight mercaptans but these compounds, while imparting the distinctive hot asphalt smell due to their volatility, are present in very low concentrations in freshly generated asphalt fumes (Gamble et al., 1999; Fraunhofer, 2003)

Asphalt fumes

Asphalt fume is a visible airborne condensation product of lower boiling volatile components of petroleum asphalt that may be inhaled or deposited on skin and clothing. When asphalts are heated to facilitate paving or roofing applications, the lighter, more volatile components are distilled into the atmosphere. As these components cool, they condense forming small droplets of liquid (fume), some of which have an effective diameter of less than 12.5 microns and are considered respirable (AI, 1990b; Brandt et al., 1985). The concentration of the lower molecular weight components of petroleum asphalts that include the tumorigenic 3-7 ring PAC in fume condensate is likely to be higher than in the parent asphalts and hence the tumorigenic potential may be increased. The temperature of fume generation affects both the relative proportions of individual PACs in the fume and the amount of fume generated. The temperature-induced variations in fume composition and amount of fume generated have significant toxicological implications as described below. It has been reported that 80-fold more fume is given off at 250^oC (482^oF) than at 160^oC (320^oF), hence appropriate temperature control can considerably reduce emissions of PAC/PAHs from asphalts (CONCAWE, 1992).

Asphalt fumes generated under a range of heating conditions have been tested by inhalation, by dermal application as a fume condensate, and *in vitro*. Generating conditions significantly affected toxicological results. Asphalt fumes generated experimentally at high temperature are more likely to contain carcinogenic PAC than fumes generated at the lower temperatures usually seen in field samples (McCarthy et al, 1999; NIOSH, 2000). Fume generation intervals have been reported to range from 4-16.5+ hours (Niemeier et al., 1988) or approximately 6 hours (AI, 1990) to produce sufficient fume for testing. Asphalt heated to 600^oF (316^oC) may undergo some thermal cracking [e.g. removal of long alkyl chains, making aromatic compounds smaller and more bio-available], generating more PAC in fume. Longer duration heating at or above 450^oF (232^oC) may lead to volatilization of constituents not found in field samples, and possible chemical reactions that do not occur in field operations (AI, 1990a).

Asphalt products are required to be heated to maintain fluidity during bulk transportation and storage. This work practice results in the potential generation of toxicologically significant concentrations of H₂S that can selectively accumulate in the vapor spaces of storage tanks and

bulk transport compartments. While creating a potential for acute overexposure to H₂S during gauging and unloading operations, i.e., exceedence of the 15 minute Short Term Exposure Limit (STEL) of 15 ppm, (ACGIH, 2003), the relative concentration of H₂S in relation to total particulate matter (TPM), benzene soluble matter (BSM) and polycyclic aromatic hydrocarbons (PACs) in freshly generated asphalt fume is insignificant (Gamble et al, 1999; Fraunhofer, 2003).

CATEGORY RATIONALE

The asphalt category comprises a single group of the heaviest, residual streams from the high temperature vacuum distillation of petroleum. These complex combinations of hydrocarbons boil above 400-550^oC (752-1021^oF) have high molecular weights and high viscosity, in order to meet the use specifications in commercial asphalt formulations. These materials display, in general, similar limited bioavailability and toxicological properties.

EVALUATION OF EXISTING HEALTH EFFECTS DATA AND PROPOSED TESTING

Introduction

Toxicity data has been developed from both whole asphalt and asphalt fumes. Actual toxicity and bioavailability of asphalts are generally quite low because of high boiling point and high molecular weight, substantial alkylation of the PAC fraction, very high viscosity, and very low water solubility. Whole petroleum asphalts possess little tumorigenic potential when applied to mouse skin, although a weak response may be seen if applied as a solution in an organic solvent, as a cut-back sample, as a paint formulation, or as a hot liquid (NIOSH, 2000; IARC, 1985; AI, 1990b).

Most toxicology studies performed on asphalt or asphalt fumes have used finished products. Although roofing and paving asphalts vary in physical properties and distribution of chemical constituents to meet use specifications, these compositional distinctions are not relevant to the toxic potential of asphalts. Toxic effects of neat asphalt or asphalt fumes correlate with the presence of biologically active 3-7 ring PACs (Roy et al., 1988, 1996). The concentration of 3-7 ring PACs in a test sample can be enhanced by extraction of neat asphalt, or by intense generation of asphalt fumes at high temperatures with subsequent condensation. Under conditions of normal use, asphalt and asphalt fumes have low levels of biologically active 3-7 ring PAC. The importance of 3-7 ring PAC in toxicity of petroleum has been demonstrated for crude oil and other categories of petroleum materials with boiling points at or above 500^oF (262^oC), which are the subjects of other HPV test plans. Indeed, because asphalts are the highest molecular weight materials on the petroleum distillation continuum, their toxic potential can be estimated from results of studies on aromatic extracts and heavy refinery streams based on the content of 3-7 ring PAC extracted with DMSO, with correction for absorption (skin penetration) caused by higher viscosity of asphalts (Potter et al., 1999). Asphalt-induced toxicity can be increased if aromatic extracts, clarified slurry oil, straight run vacuum distillates, or coal tar are used as blending materials to meet product specifications.

Worker monitoring and epidemiology studies provide “real world” results from exposure to asphalt and asphalt fumes, but significance of results of these studies for asphalt-specific health effects are sometimes complicated by the presence of coal tars in the asphalt blends, other potential toxicants at the work sites (e.g. diesel fuel exhaust, benzene, fiberglass), smoking and life style factors. Human data relating to acute exposure has been cited to supplement available animal data, but robust summaries have not been prepared.

Study Review and Evaluation

Results of studies on roofing and paving asphalts are summarized in this section. Laboratory studies have focused primarily on carcinogenesis of asphalt and asphalt fumes and on genetic toxicity studies which are predictive of carcinogenesis. However, systemic toxicity can be determined from the available repeated dose studies and supported by the results of chronic toxicity/carcinogenesis bioassays. Where animal data are limited, results from adequate human monitoring studies, and extrapolation of results from studies of related materials will be considered to address the endpoint of interest. Detailed study information is available in the Robust Summaries organized in the IUCLID data set format employed by the European Union (Appendix 4). The currently available data submitted to the HPV program and any additional testing will be developed with the goal of facilitating international harmonization of hazard and risk characterization worldwide.

Acute Toxicity

Acute oral and dermal toxicity studies on two vacuum residuum samples, API 81-13 and API 81-14 [CAS #647-56-6](API 1982a, b) demonstrated that asphalts did not induce significant acute toxicity by the oral route in rats [LD50 >5.0g/kg] although hypoactivity, diarrhea and dark stained anal region were observed, or by the dermal route in rabbits [LD50 >2.0g/kg]. In rabbits, slight dermal irritation was observed [Irritation Index = 0.2 for API 81-13; 0.4 for API 81-14] and mild to moderate eye irritation in both washed and unwashed eyes was observed at 24 hours (API, 1982a, b). Dermal treatment of guinea pigs with undiluted, heated vacuum residuum samples did not induce sensitization (API, 1984a, b).

Male and female Wistar WU rats were exposed to fumes generated from condensate collected in the headspace of a bitumen storage tank, by nose-only inhalation for 4.5 hours according to OECD guideline 403 at a target concentration of 100mg/m³ (Fraunhofer ITA, 2000). Mean actual exposures measured by IR spectroscopy according to BIA (Germany) guideline #6305 and corrected for aromatics by a factor of 1.9 were 25.5mg/m³ for the first 30 minutes (65mg/m³ x 1.9) and 182.2mg/m³ (94.4mg/m³ x 1.9) for the subsequent 4 hours. No mortality or toxicity was observed, except for slightly lower body temperatures at the end of exposure.

Acute effects among workers exposed to asphalt fumes included eye irritation, and nasal and throat irritation which typically appeared to be of mild severity and transitory in nature (Gamble et al., 1999; NIOSH, 2000). Dermal exposure to many neat asphalt formulations is limited, in that these materials are handled hot (180-450 F) and even brief exposure will cause immediate skin burns. Skin irritation has been reported after exposure to asphalt based materials (cold product or fume) but results may be confounded by co-exposure to diesel fuel, diesel exhaust, coal tar or fiberglass, and environmental conditions (Chase, 1994; Tavis et al, 1984; NIOSH, 2000).

Summary: Results of animal studies and human monitoring indicate that acute toxicity of asphalts and asphalt fumes is low and effects are transitory. **No additional acute toxicity testing is proposed.**

Repeated Dose Toxicity

In two dermal toxicity studies, rabbits were treated with 200, 1000, and 2000mg/kg vacuum residuum samples API 81-13, API 81-14, undiluted and occluded, once a day, 3 times a week for 4 weeks. At 2000mg/kg, rabbits appeared thin, experienced decreased body weight gain, and decreased food intake. Flaking skin, acanthotic dermatitis and hyperkeratosis were seen in males

given 2000mg/kg API 81-13, and in both sexes, API 81-14 also produced wart-like lesions and white discharge at the treated site. No systemic toxicity was reported (API, 1983a, b).

Inhalation (nose-only) exposure of male and female Wistar rats to asphalt fume condensate collected over a paving asphalt tank was performed for 90 days at target concentrations of 0, 4, 20, and 100mg/m³ according to OECD guideline 413 (Fraunhofer ITA, 2002a). Actual mean concentrations measured by IR according to BIA [Germany] guideline #6305 and corrected for aromatic content (Ekström et al., 2001), were 5.53, 28.17, and 149.17mg/m³ total hydrocarbon of bitumen fumes. At 149.17mg/m³, male rats exhibited statistically significant lower body weights with a concurrent decrease in food consumption, and female rats had slightly lower body weights than controls. Histopathological changes were observed in the nasal and paranasal cavities in both sexes that consisted of slight to moderate occurrence of hyalinosis and some mucosal cell hyperplasia at the top exposure level. Broncho-alveolar lavage demonstrated a statistically significant increase in mean cell concentration, lactate dehydrogenase levels and alpha glutamyl transferase levels in high dose female rats; effects in high dose males were similar but less pronounced. The NOAEL for this study was 28.17mg/m³.

Summary: Subchronic toxicities of asphalt and asphalt fumes are likely to be low and restricted to irritant effects in the skin or in the nasal passages and lungs, depending on the route of exposure. From the studies described here and the substantial body of data from chronic/carcinogenicity studies cited below and presented in detail in Robust Summaries, additional repeated dose toxicity studies of 90 days or less are unlikely to provide substantial new data. **No repeated dose toxicity testing is proposed.**

Carcinogenicity

Long-term studies have been performed on various types of asphalts by skin contact with asphalt itself or with condensed fumes, or inhalation of fumes generated when asphalts are heated. These studies are summarized in Appendix 4 to provide a complete review of asphalt toxicity data. Robust summaries were not prepared since carcinogenicity studies are not part of the HPV program.

Summary: Undiluted asphalts of any type are not carcinogenic by dermal exposure and dilution of asphalts with organic solvents may induce none to weak dermal tumorigenesis over a long duration of treatment. Skin-painting studies do indicate that asphalt fumes generated under laboratory conditions produce skin tumors in mice. However, the analytical comparisons of field- and laboratory-generated asphalt fumes indicate that they are compositionally dissimilar. In studies performed by NIOSH (Niemeier et al., 1988; Sivak et al., 1989, 1997), asphalts were heated to higher temperatures for significantly longer periods of time than under field conditions, in order to generate sufficient fumes for testing. Thermal cracking, volatilization of constituents not released from asphalts under workplace conditions and other chemical reactions inconsistent with “real world” usage, make the results of these studies unrepresentative of the workplace hazard to man.

Exposure of laboratory rodents (Mice, rats or guinea pigs) induced non-specific respiratory irritation, bronchitis and pneumonitis but no evidence of lung or other systemic cancers. (Heuper and Payne, 1960; Simmer, 1964)

In Vitro Genetic Toxicology

Bacterial mutagenicity assays: The testing of whole asphalts diluted or extracted with organic solvents resulted in no mutagenicity or weak mutagenic activity only with metabolic activation

(rodent S-9 liver homogenate) in *Salmonella typhimurium*. Penalva et al. (1983) found weak activity for a dimethylsulfoxide (DMSO) extract of road tar (that may have contained coal-derived material) with S-9, while Monarca et al (1987) reported that DMSO extracts of three asphalt samples were not mutagenic in the *Salmonella* assay, nor were extracts from airborne particulates collected during road paving operations, even using a 5-fold increased S-9 mixture. Four samples of asphalt-based paints [60% asphalt cut back with mineral spirits] were inactive in *Salmonella* with or without S-9 microsomal activation (Robinson et al., 1984). Blackburn and Kriech (1990) reported marginally positive findings with DMSO extracts of roofing and paving asphalts in the Modified Ames assay using elevated levels of S-9. Fume condensates, derived from heating these asphalts to temperatures greater than 232°C (450°F) were moderately active, and comparably generated fumes from coal tar pitch were greater than 1000 times more active. When paving asphalt was heated to a temperature more representative of that in practical use, 163°C (325°F), very little fume was generated and mutagenicity was much lower.

The National Toxicology Program evaluated the mutagenic potential of asphalt fume condensates and fractions prepared by Sivak et al., (1989) for dermal carcinogenicity studies, by heating Type III roofing asphalt to 316°C (601°F) to generate fumes. The fumes were fractionated into 5 fractions (A-E) using HPLC. The unfractionated fume condensate and fractions B and C [containing PAC] were weakly positive; fraction E, comprised primarily of C6-C22 alkylated ketones, alkylated naphthols and phenols, was negative, and the recombined A-E fraction was positive with metabolic activation (NTP, 1990). The same fractions tested by Blackburn and Kriech (1990) gave similar results using the Modified Ames test. Machado et al. (1993) evaluated the mutagenic activity and PAH content of laboratory generated fumes from two Type III roofing asphalts from different crude oils [fumes generated at 232°C(450°F) or 316°C (601°F)], 18 paving asphalts from 14 different crude oil sources and various processing conditions [fumes generated at 163°C (325°F)], and one Type I coal tar pitch [fumes generated at 232°C(450°F) or 316°C (601°F)]. All asphalt samples showed weak to moderate mutagenic response in the Modified Ames test, responses approximately 100-fold less than the mutagenicity of the coal tar pitch sample. Reinke and Swanson (1993; Reinke et al., 2000) also compared chemistry of PAH and sulfur containing PAC and mutagenic potential in the Modified Ames test, of field and laboratory generated asphalt fume condensates from asphalt cement. Field samples were collected from headspace of an asphalt storage tank at 146-157°C (295-315°F) and laboratory samples were generated at 149°C or 316°C. Field samples showed minimal mutagenicity [MI>0 and <1] and laboratory fumes generated at 149°C [MI 5.3] and 316°C [MI 8.3] were clearly mutagenic. Authors noted positive trends between mutagenicity and the percentage of 3-ring and greater PAH and S-PAC, and postulated that the higher mutagenicity of fumes generated at 316°C could be attributed to increased concentration of 4-ring S-PAC. DeMéo et al. (1996) made similar comparisons in the Modified Ames test for fumes of coal tar and two paving asphalts generated at 160°C and 200°C (320°and 392°F), and found all fumes mutagenic in *Salmonella* with metabolic activation. Coal tar fume condensates induced mutagenic potency was 15-600 fold higher than that from asphalt fume condensates. All fume condensate samples also induced DNA adducts in calf thymus DNA *in vitro*. No specific adducts were identified and the pattern of autoradiograms of DNA demonstrated qualitative differences in the nature of adducts induced by asphalt or coal tar fume condensates.

Mammalian cell mutation assays: Two vacuum residuum samples (API 81-13, API 81-14; CAS #64741-56-6) were solubilized in DMSO and tested in the L5178Y Mouse lymphoma cell mutagenesis assay. Both vacuum residuum samples were not mutagenic without metabolic activation but were weakly active in the presence of S-9 mixture in the range of low to moderate mammalian cell toxicity (API, 1983d,e).

Chromosome aberration assays: Condensates of Type I and Type III roofing asphalt fumes, and fractions of these condensates generated in the laboratory at 316^oC (601^oF) by the method of Sivak et al. (1989) caused a dose-related increase in micronucleus formation in Chinese Hamster lung fibroblasts (V79) cells (Qian et al., 1996, 1999), primarily by spindle apparatus alteration in dividing cells. However, three paving asphalt fume condensates generated in the field and in the laboratory were negative in an unspecified chromosome aberration assay (Reinke and Swanson, 1993; Reinke et al., 2000).

Summary: *In vitro* studies demonstrate that whole asphalts are non-mutagenic or weakly mutagenic, and that fume condensates are mutagenic with the severity of the effect correlated with the temperature under which fumes are generated. **No additional *in vitro* genetic toxicity tests are proposed.**

In Vivo Genetic Toxicology

Vacuum residuum samples (API 81-13; API 81-14) were administered orally to Sprague Dawley rats at doses of 0, 0.3, 1.0, or 3.0g/kg/day for 5 days. No chromosomal abnormalities were seen in bone marrow cells after 5 days of exposure (API, 1983c,d).

Ma et al. (2002) exposed rats intratracheally for 3 consecutive days to asphalt fumes condensates collected at the top of a paving storage tank at temperature of 160^oC (320^oF) at doses of 0 (saline), 0.45, 2.22 or 8.88mg/kg/day. Exposure to 8.88mg asphalt fume condensate/kg rat body weight cause a statistically significant increase in the level and activity of CYP1A1, a major isozyme of cytochrome P450, in the lung, and increased micronucleus formation in bone-marrow polychromatic erythrocytes (PCE). The incidence of micronuclei was evaluated only at the low and high dose. The increased level of micronuclei at 8.88mg/kg was accompanied by a statistically significant decrease in PCE/1000 erythrocytes, indicative of cell toxicity, which may have affected the micronuclei incidence, and thus potentially confounded results. The investigators attributed the effects to bio-activation of the PAC present in the asphalt fumes. However, in a study of non-smoking Swedish road pavement workers exposed to asphalt fumes generated at application temperatures, Jarvholm et al. (1999) found no increase in sister chromatid exchanges or micronucleus formation in peripheral blood lymphocytes.

In vivo DNA adduct studies in rats and mice using the ³²P-postlabeling technique demonstrated induction of a variety of adducts by asphalt fume condensates but no specific adducts were identified. Genevois et al. (1996) performed an *in vivo* study as a follow-up to the *in vitro* study of DeMéo et al (1996) described above. They demonstrated adduct formation in skin, lungs and lymphocytes of rats dermally treated with asphalt or coal tar fume condensates in different patterns. HPLC analyses of the condensates indicated that coal tar fume condensate contained large amounts of unsubstituted PAH, which were only minor constituents of asphalt fume condensate. Multiple applications of asphalt based paints to the backs of mice resulted in accumulation of adducts in skin and lung tissue, but again, no specific adducts were identified (Schocket et al., 1988). Qian et al. (1998) using the ³²P- post-labeling method, measured DNA adduct levels induced by Type I or Type III roofing asphalt fume condensate instilled in the lungs of male CD rats at concentrations of 250, 500, 1000 or 2000mg/kg body weight, 3 times at 8 hour intervals. Fume was generated from asphalt heated to 316±10^oC by the method of Sivak et al., 1989. DNA adduct levels were increased compared to controls in the lungs of rats treated with Type I asphalt at or above 500mg/kg, and at 250mg/kg for Type III asphalt. The migration pattern of DNA adducts was similar for both asphalts. However, there was no elevation in DNA adduct levels in leukocytes collected by cardiac puncture from the same rats.

Summary: *In vivo* genetic toxicity data included two negative oral chromosome aberration studies on vacuum residuum samples, a micronucleus test in which asphalt fume condensate instilled intratracheally induced increased micronucleus formation in bone marrow erythrocytes, and positive dermal and intra-tracheal instillation DNA adduct tests. The positive micronucleus results observed with intra-tracheal instillation of asphalt fume condensate differ from the absence of cytogenetic effects observed with dermal exposure to other refinery streams that contain a higher level of biologically active PAC [e.g. clarified slurry oil; Pryzgodna et al., 1999] than are present in asphalt and asphalt fumes, and from the absence of effect in road paving workers (Jarvholm et al., 1999). The conflicting results in the *in vivo* cytogenetic assays presented above should be resolved by the micronucleus evaluations (at 5 days, 30 days, 3 and 12 months) being conducted in rats exposed to bitumen fumes at concentrations of 5, 20 and 100 mg/m³, 6 hours/day, 5 days/week for 104 weeks in an ongoing lifetime inhalation study (Fraunhofer ITA, 2002b). **No additional *in vivo* genetic toxicity test is proposed.**

Reproductive/Developmental Toxicity

No developmental or reproductive toxicity studies on asphalts or asphalt fumes are available. However, considering the high molecular weight, limited bioavailability and minimal observed general toxicity of whole asphalts, they are unlikely to cause developmental or reproductive effects. Since the toxicity from asphalt fumes appears correlated with the concentration of 3-7 ring PAC in the condensate, as it does with other petroleum streams boiling above 500⁰F (262⁰C), it should be possible to estimate the potential for reproductive/developmental toxicity from results of studies already performed with aromatic extracts and heavy fuel streams which are the subjects of other HPV test plans. **To provide definitive data for extrapolation to workers potentially exposed to asphalt fume, a reproductive/developmental toxicity-screening test (OECD 421) is proposed by the inhalation route of exposure.**

EVALUATION OF EXISTING PHYSICOCHEMICAL AND ENVIRONMENTAL FATE DATA

The physicochemical endpoints for the EPA HPV chemical program include melting point, boiling point, vapor pressure, water solubility, and octanol/water partition coefficient (K_{ow}). Environmental fate endpoints include biodegradation, photo-degradation, hydrolysis, and fugacity. Because the HPV substances covered under the testing plan are mixtures of differing compositions, it is not possible to measure or calculate a single numerical value for some of the physicochemical properties. For example, a product that is a mixture of chemicals does not have a melting point, but rather a melting point range. Therefore, values for some physicochemical properties will be represented as ranges of values according to the product's component composition. Although some data for products in this category exist, not all of these endpoints are defined and a consensus database for chemicals that represent products in this category does not exist. Therefore, calculated and measured representative data will be identified and a technical discussion provided where appropriate. The EPIWIN[®] computer model (EPA, 2000), as discussed in the US EPA document entitled "The Use of Structure-Activity Relationships (SAR) in the High Production Volume Chemicals Challenge Program" is used to calculate some of the physical/chemical properties of representative constituents for selected production streams within the Asphalts and Vacuum Residues Category.

Physicochemical Data

Melting Point

Asphalts are viscous semi-solid to solid materials at ambient temperatures that do not have sharply defined melting points. They gradually become softer and less viscous as the temperature rises. For this reason, the softening point is commonly used as a means of standardizing the classification of the flow characteristics of asphalts (ASTM, 2000). A range of softening points, as measured by ASTM Method D36, of a penetration grade (CAS No. 8052-42-4), a hard grade (CAS No. 8052-42-4) and an oxidized grade (CAS No. 64742-93-4) of asphalts were reported by CONCAWE (1992) as 30 to 60 °C, 60 to 75 °C and 60 to 130 °C, respectively.

Summary: No testing is proposed. The melting characteristics of asphalt substances have been adequately described.

Boiling Point

Asphalt and vacuum residue are obtained as the residues from the vacuum distillation of crude oil. CONCAWE (2001) reported a typical boiling range of >450 °C. This is consistent with values given in CONCAWE (1992) and API (1987) for various product streams of these materials.

Summary: No testing is proposed. The boiling range for asphalt and vacuum residue has been adequately characterized.

Vapor Pressure

Substances in the asphalt category are semi-solid to solid materials, boil at temperatures above 450°C, and have negligible vapor pressure at ambient temperatures (CONCAWE, 2001).

Summary: No testing is proposed. The vapor pressure for asphalt and vacuum residue has been adequately characterized.

Partition Coefficient

Substances in the asphalt category are semi-solid to solid at ambient temperatures and have negligible vapor pressure and water solubility (CONCAWE, 2001). Modeling the partition coefficients of representative hydrocarbon structures having 25 carbon atoms using the EPIWIN computer model (EPA, 2000) showed estimated partition coefficients to be typically >10. Therefore, these complex mixtures will not have measurable partition coefficients using standard testing methodologies (OECD, 1993).

Summary: No testing is proposed. Estimated partition coefficients of representative C25 constituent hydrocarbons are >10.

Water Solubility

Substances in the asphalt category consist of hydrocarbons having 25 or more carbon atoms and molecular weights of 500 to 15000. At room temperature, these substances exist as semi-solid to solid materials and as such they are expected to have extremely low water solubility (CONCAWE, 1992 and 2001). However, since materials in this category are often employed in waterproofing applications (NIOSH, 2000), there is a potential to leach components from the asphalt into the water. Brandt and De Groot (2001) studied the PAH compounds in static leachate water from nine

bitumens (asphalts). They found trace amounts of petroleum hydrocarbons, naphthalene being the most prevalent in concentrations ranging from 1 to 400 ng/l (parts per trillion), while PAHs having three and four rings ranged from 0.1 to 180 ng/l and 0.1 to 5 ng/l, respectively. In a similar trial, the Asphalt Institute (2003) found very low but, measurable concentrations of naphthalene in fresh hot mix asphalt leachate water (250 ng/l). Other PAHs were all below detection limit concentrations [detection limits ranged from 15-194ng/l]. Measurements of other semi-volatile and volatile compounds were not detected. Of eight metals measured, only chromium was detected at a concentration of 0.1 mg/l. The chromium was also present in the blanks and originated from the bichromate/sulfuric acid used for cleaning the glassware (Brandt and De Groot, 2001; Bowen, De Groot and Brandt, 2000).

Analysis of 29 polycyclic aromatic compounds (PACs) has also been performed on 10 different asphalts (Kriech, 2002). The U.S. EPA under the Emergency Planning and Community Right-to-Know Act (EPCRA) section 313 requires reporting of twenty of these compounds. Results showed no detectable levels (<100 ng/l) of any of these PACs. Naphthalene and phenanthrene were detectable in two of the asphalts, with results consistent with the above data, but well below drinking water limits.

Summary: No testing is proposed. The water solubility of asphalt and vacuum residue has been adequately characterized.

Environmental Fate Data

Environmental fate data for the Asphalt category that can be used in the HPV chemicals program were not found. The following describes the fate endpoints and the type of information that will be developed.

Photodegradation

Asphalt and other compositionally similar materials found in this category are composed of high molecular weight hydrocarbon molecules containing 25 or more carbon atoms. At ambient temperatures these substances exist as semi-solid to solid materials having negligible vapor pressure and water solubility. These physical/chemical features limit their distribution in the environment. Although constituent hydrocarbons present in the asphalt process streams in this category are not expected to partition to air or dissolve in water, when heated during road-surfacing and roofing applications, fumes and vapors are created (NIOSH, 2000). Fumes will condense when cooled, but residual vapor may be transported and dispersed in the atmosphere. When this occurs, hydrocarbon molecules may undergo direct or indirect photo-degradation depending on the extent to which they are transported and their exposure to conditions conducive to those reactions. Some asphalt constituents are polyaromatic compounds, which have been shown to absorb light energy in the 290 to 800 nm range where direct photolytic reactions may result. However, absorption is not always sufficient for a chemical to undergo photochemical degradation. The degree and rate at which these compounds might engage in direct photo-degradation reactions depends upon penetration of light with sufficient energy to effect a chemical change. Indirect photo-degradation may occur in the atmosphere when organic compounds interact with photo-chemically produced hydroxyl radicals, ozone or nitrogen oxides. Saturated hydrocarbon compounds react readily with OH and NO₃ radicals, and monoaromatic and diaromatic compounds react with OH radicals to undergo degradative reactions (Atkinson, 1990).

Although individual hydrocarbon molecules present in the asphalt category have the capability to undergo direct or indirect photo-degradation reactions, the significance of this fate process is

expected to be minimal. At ambient temperatures, asphalts will exist as semi-solid to solid substances with negligible water solubility and vapor pressure thus limiting their dispersal and photo-degradation in the environment.

Summary: No testing or modeling is proposed. The physicochemical characteristics of substances in this category do not favor distribution to environmental compartments where photo-degradation reactions will occur.

Stability in Water

Hydrolysis of an organic chemical is the transformation process in which a water molecule or hydroxide ion reacts to form a new carbon-oxygen bond. Chemicals that have a potential to hydrolyze include alkyl halides, amides, carbamates, carboxylic acid esters and lactones, epoxides, phosphate esters, and sulfonic acid esters (Harris, 1982). Materials in the Asphalt HPV Category are not subject to hydrolysis.

Summary: Computer modeling will not be conducted for materials in the Asphalt HPV Category because they do not undergo hydrolysis.

Chemical Transport and Distribution in the Environment (Fugacity Modeling)

Substances in the Asphalt HPV Category contain some of the heaviest and least volatile fractions of petroleum (US EPA, 1985). At ambient temperatures they exist as semi-solid to solid substances with negligible vapor pressure and negligible water solubility. Because the physicochemical characteristics of these substances limit their capacity to distribute to different environmental media, a brief technical discussion will include a general description of the composition and chemical structure for these materials, and scenarios whereby these materials may be used in the environment.

Summary: Computer modeling will not be conducted for substances in the Asphalt, and Vacuum Residue HPV Category because their high molecular weights and physicochemical characteristics preclude them from dispersing in the environment. Instead, a technical discussion on the potential environmental distribution of these materials will be prepared and added to IUCLID, which is the electronic database that will contain data for the HPV chemicals program.

Biodegradation

Biodegradation is the utilization of a chemical by microorganisms as a source of energy and/or carbon. The parent chemical is broken down to simpler, smaller chemicals, which are ultimately converted to an inorganic form such as carbon dioxide, nitrate, sulfate, and water. Assessing the biodegradability of chemicals using a standard testing guideline can provide useful information for evaluating chemical hazard. Biodegradation can be measured using the OECD test guidelines 301A-F or 302A-C (OECD, 1993). However, because of their structure and physical state, materials in the Asphalt category would not be subject to bio-degradative processes that would be measurable with standard testing guidelines. However, substances in this category have shown some susceptibility to biodegradation by a few microbial species. Various microorganisms have been isolated that are able to utilize asphalt as a source of carbon for growth. For example, Phillips and Traxler (1963) demonstrated that species of *Pseudomonas*, *Chromobacterium*, and *Bacillus* were capable of degrading thin films of asphalt painted on culture flasks. Degradation between 3 and 25% were measured after one week of incubation, and in one experiment measured 90% after one month. Fluctuations in temperature, pH, and oxygen tension affected to a greater or lesser degree the ability of these microorganisms to biodegrade asphalt (Phillips and Traxler 1963; Cundell and Traxler, 1973).

Although hydrocarbon components in asphalt appear capable of being biodegraded, degradation rates are greatest under laboratory conditions where the surface area available for microbial contact was maximized and other physicochemical conditions optimized for greatest effectiveness (ZoBell and Molecke, 1978). Under realistic exposure conditions, where the bulk properties of asphalt limit dispersion and the available surface area for microbial exposure, biodegradation is expected to be minimal.

Summary: Biodegradation testing will not be conducted for materials in the Asphalts and Vacuum Residue Category because they are not likely to biodegrade under standard testing conditions. Instead, a technical discussion on the potential of these materials to degrade will be prepared and added to IUCLID, which is the electronic database that will contain data for the HPV chemicals program.

Evaluation of Existing Ecotoxicity Data and Proposed Testing

The environmental effects endpoints in the HPV Challenge program include:

- Acute Toxicity to Fish,
- Acute toxicity to Aquatic Invertebrates, and
- Toxicity to Algae (Growth Inhibition)

There are no standard testing guideline studies on the toxicity of asphalt or vacuum residue to these aquatic organisms, but contaminants in surface water runoff from in-place pavements have caused concern for potential environmental impacts to receiving water bodies (Buckler and Granato, 1999). Chemical analyses have shown that runoff from pavements contains a multitude of chemicals including deicers (Adams-Kszos *et al.*, 1990; Crowther and Hynes, 1977), metals (Maltby *et al.* 1995; Adams-Kszos *et al.*, 1990; Moore and Butler, 1994), and organic compounds (Dupuis *et al.* 1999; Maltby *et al.* 1995; Horner and Mar, 1985). However, these chemicals typically originate from vehicle emissions, spills/droppings of crankcase oil, deicers, nutrients, pesticides/herbicides, fuel additives, maintenance materials and catalytic converter emissions (Buckler and Granato, 1999). Hence, adverse impacts to water bodies receiving pavement runoff are likely to result from those types of constituents rather than from leachate from asphalt itself. In fact, studies have shown non-detected or very low concentrations (e.g., ng/l levels) of hydrocarbons and inorganic elements originating from asphalt leachate (Asphalt Institute 2003; Brandt and De Groot, 2001).

Asphalt and vacuum residue are not expected to cause acute or chronic toxicity to aquatic organisms due to the extremely low water solubility of these materials. Asphalt linings have been applied to aquaculture ponds in Oregon and Washington with no apparent adverse impact to the culture and propagation of sport and food fish (Schlect, 1991). Evidence for a lack of aquatic toxicity also is shown using data on other petroleum products having similar types of hydrocarbon constituents (i.e., saturate and aromatic fractions). For example aromatic extracts, which contain a large proportion of polyaromatic hydrocarbons of C15 – C54, showed no acute or chronic toxicity in aquatic organisms (CONCAWE, 2001). Similarly, lubricating oil basestocks, which contain saturate as well as aromatic hydrocarbons of C15 – C50, showed no acute or chronic toxicity in aquatic organisms (CONCAWE, 1997; API, 2003). These data are shown in Table 3, below. Asphalt and vacuum residue, with saturate and aromatic hydrocarbon molecule of C25 and higher, also would not be considered sufficiently water soluble to elicit acute or chronic toxicity in aquatic animals and plants.

Table 3. Representative Ecotoxicity Data for Lubricating Base Oils and Aromatic Extracts.

	Fish Acute/Prolonged Toxicity	Invertebrate Acute Toxicity	Algal Toxicity	Invertebrate Chronic Toxicity
Lubricating Base Oils ¹	96-hour LL0 = 1000 mg/L 7-day LL0 = 1000 mg/L	48-hour EL0 = 1000 mg/L	96-hour NOEL = 1000 mg/L	
Aromatic Extracts ²	96-hour LL0 = 1000 mg/L	48-hour EL0 = 1000 mg/L	72-hour NOEL = 1000 mg/L	21-day NOEL = 1000 mg/L

(E)LL0 = Test substance loading concentration at which no mortality or effects existed.

NOEL = No observed effect level.

¹ CONCAWE 1997

² CONCAWE 2001

Summary: No testing is proposed. The constituent hydrocarbons making up asphalt and vacuum residue are of such high molecular weight and low solubility that such materials would not be expected to cause acute or chronic toxicity in aquatic organisms. This is supported by data from other petroleum hydrocarbon streams having similar hydrocarbon structures.

TABLE 4. MATRIX OF AVAILABLE ADEQUATE DATA AND PROPOSED TESTING FOR SELECTED TEST MATERIAL

Test	Asphalt
Melting Point	Adequate
Boiling Point	Adequate
Vapor Pressure	Adequate
Partition Coefficient	Model complete
Water Solubility	Adequate
Photo-degradation	NA [Discussion]
Stability in Water	NA [Discussion]
Transport and Distribution	NA [Discussion]
Biodegradation	NA [Discussion]
Acute Toxicity to Fish	Adequate; Read across [C]
Acute Toxicity to Aquatic Invertebrates	Adequate; Read across [C]
Toxicity to Algae	Adequate; Read across [C]
Acute Toxicity	Adequate
Repeated Dose	Adequate
Genotoxicity, <i>in vitro</i>	Adequate
Genotoxicity, <i>in vivo</i>	Adequate
Repro/ Developmental	Test

Adequate Indicates adequate existing data.
 Test Indicates proposed testing
 Model Indicates data will be obtained with EPA approved models
 C Indicates category read-across from existing or proposed test data
 N/A Indicates that evaluation of endpoint is Not Applicable due to physical-chemical state or route of administration. Technical discussions will be developed to address these endpoints as appropriate.

There are no studies available on the developmental and reproductive toxicity potential of asphalts. Therefore, this study plan proposes a reproductive/developmental toxicity-screening test in rats (OECD 421). Test material will be a representative sample of current production asphalt fume that is generated by a method that ensures exposure reflective of real world conditions and administered via inhalation. No additional environmental studies are proposed. Results of these studies combined with available results on asphalts, and compositionally and toxicologically similar heavy refinery streams addressed in other test plans will be adequate to complete the hazard profile for streams in this category.

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APPENDIX 1: ASPHALT HPV CATEGORY

Asphalt, CAS #8052-42-4.

A very complex combination of high molecular weight organic compounds containing a relatively high proportion of hydrocarbons have carbon numbers predominantly greater than C25 with high carbon-to-hydrogen ratios. It also contains small amounts of various metals such as nickel, iron, or vanadium. It is obtained as the non-volatile residue from distillation of crude oil or by separation as the raffinate from a residual oil in a deasphalting or decarbonization process.

Residues (petroleum), vacuum, CAS #64741-56-6.

A complex residuum from the vacuum distillation of the residuum from atmospheric distillation of a crude oil. It consists of hydrocarbon having carbon numbers predominantly greater than C34 and boiling above approximately 495°C (923°F).

Raffinates (petroleum), residual oil decarbonization, CAS #64742-07-0.

A complex combination of hydrocarbons obtained as the solvent insoluble fraction from C5-C7 solvent decarbonization of a residual oil. It consists predominantly of aromatic hydrocarbons having carbon numbers predominantly higher than C34 and boiling above approximately 495°C (923°F).

Petroleum Resins, CAS #64742-16-1.

A complex combination of organic compounds, predominantly hydrocarbons, obtained as a fraction of the extract of solvent extraction of residuum. It consists predominantly of high molecular weight compounds with high carbon-to-hydrogen ratios.

Residues (petroleum), hydrodesulfurized vacuum, CAS #64742-85-4.

A complex combination of hydrocarbons obtained by treating a vacuum residuum with hydrogen in the presence of a catalyst under conditions primarily to remove organic sulfur compounds. It consists of hydrocarbons having carbon numbers predominantly greater than C34 and boiling above approximately 495°C (923°F).

Asphalt, oxidized, CAS #64742-93-4.

A complex black solid obtained by blowing air through a heated residuum, or raffinate from a deasphalting process with or without a catalyst. The process is principally one of oxidative condensation which increases the molecular weight.

APPENDIX 2: ASPHALT MANUFACTURE [CONCAWE, 1992; IARC, 1985]

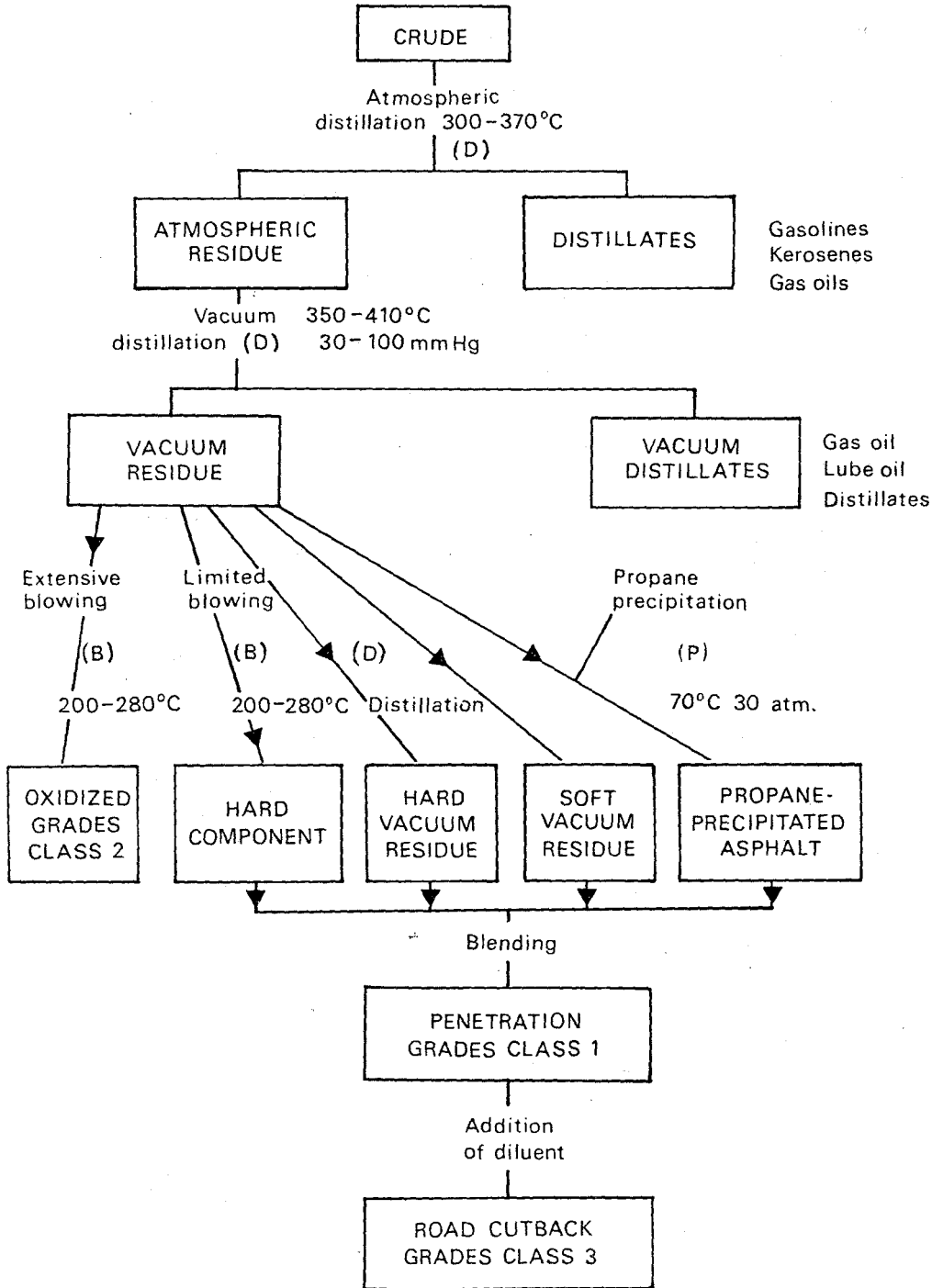
Asphalts are produced from petroleum crude oils by low temperature non-destructive refining processes that remove most species boiling below 542^oC (1000^oF) and avoid high temperatures or other conditions that result in significant thermal cracking. (Figure A2-1).

- Atmospheric distillation (**D**) of crude oil at temperatures usually not exceeding 385^oC (725^oF) yields volatile fractions [e.g. gasoline, kerosene, gas oil] and heavier atmospheric residue with the consistency of fuel oil.
- Vacuum distillation (**D**) further refines the atmospheric residue to produce lubricating oil distillate fractions and a vacuum residuum. Distillation is performed at lower pressure and a temperature in the range of 380^oC (716^oF) to avoid thermal cracking. The vacuum residue from heavy crude oils may be sold as commercial asphalt, and the residue from lighter crude oils is feedstock for further processing.
- Air blowing (**B**) involves introducing air under pressure into asphalt feedstock, usually heated to 220-300^oC (428-572^oF) and sometimes in the presence of catalyst, to produce higher molecular weight compounds which give a harder, less temperature sensitive product, by oxidation and condensation polymerization. The asphaltene content is increased while the cyclic aromatic content decreases. Moderate blowing is used to obtain hard road asphalt or viscosity grade asphalts from vacuum residues. Severe treatment produces oxidized asphalts suitable for a wide range of building and industrial applications.
- Solvent precipitation (**P**) or deasphalting is employed to remove asphaltic compounds from certain vacuum residues to leave valuable high viscosity base oils (bright stocks) for lubricants. Residuum is dissolved in liquid propane or a propane/butane mixture, and the aliphatic fraction is precipitated and drawn off. Solvent precipitated asphalts have a higher content of asphaltenes than the vacuum residuum from which they are produced but a lower content of saturates than would be obtained by distillation of the vacuum residue.
- Thermal conversion reduces large paraffinic molecules to smaller ones and, to a lesser degree, a condensation occurs increasing asphaltenes and resins. The process is used primarily with residues from lighter crude oils to modify the ratios of paraffins, resins and asphaltenes. During this cracking process, some polycyclic aromatic compounds (PAC) are formed. The thermal residue is then distilled in a vacuum unit to remove volatiles including PAC and the remaining residue is used as a component of blended asphalt.

Ancillary Processes

Products from all these processes can be combined to meet performance specifications. Additional blending, cutting-back [mixing with volatile petroleum diluents], or fluxing [addition of high boiling (>350^oC) heavy distillates or industrial process oils] can provide further product flexibility.

Figure A2-1: Main Processing methods in the manufacture of asphalts



VR, vacuum residue; PPA, propane-precipitated asphalt

from IARC, 1985

APPENDIX 3: Commercial Uses of Asphalts [AI, 1990, 2003; NIOSH, 2000]

Roofing:

- 1- Roofing asphalts are graded as Type I, II, III, or IV in increasing order of hardness. These products are commonly liquefied by heating and applied directly during construction. Mopping grade roofing asphalts are used as an interply adhesive or top coating for asphalt saturated felts on built-up roofs. To insure proper performance and longevity, and to avoid product degradation due to overheating, roofing asphalts are typically heated to between 450-525°F on the job site and applied at lower temperatures of 330-445°F at the point of mopping. The slope of the roof decides the grade of asphalt used; as the slope increases so does the hardness and grade of asphalt [Table A3-1].

2-

Table A3-1. Grades and characteristics of roofing asphalts

Type	Characteristics	Typical Application Temp.
I	Low softening point; soft roofing or dead level asphalt for inclines up to 0.5 inch/ft	330-355°F (166-179°C)
II	For inclines of 0.5-1.5 inches/ft	365-390°F (185-199°C)
III	For inclines of 1-3 inches/ft	395-420°F (202-216°C)
IV	High softening point, hard roofing asphalt for inclines from 2-6 inches/ft	430-445°F (221-229°C)

Asphalt Institute, 1990

Roofing asphalts are usually manufactured by blowing air through a heated residuum [usually a vacuum residuum] with or without a catalyst.

- 2- Asphalt shingles (saturated felts, coated fabrics, coated glass fibers)
 The saturant or coating asphalt is produced by blowing air through heated residuum, which is mixed with mineral filler at the roofing plant and applied to an organic or inorganic matting to produce granule surfaced shingles, smooth surface shingles, smooth roll ply sheets or granule surfaced roll sheets.
- 3- Modified bitumen roll roofing materials
 In the roofing plant, non-blown, viscosity graded asphalt cement is heated and mixed with fillers and a polymer or copolymer which is then impregnated onto an inorganic reinforcing matting and formed as a granule surfaced or smooth surfaced roll. This material is normally installed on a roof as a multilayer membrane system.

Paving:

There are three types of asphalt products used in the building of roads and other paved surfaces.

- 1- Hot Mixed Asphalt [HMA] is a blend of asphalt paving cement and mineral aggregates. Asphalt paving cement is the straight reduced or vacuum processed asphalt used mainly as a binder (4-10%) of hot mixed asphalts to hold the aggregate together. HMA materials comprise 85% of all paving products and are the most important commercially and in terms of number of workers exposed.

- 2- Cutback asphalts are a mixture of asphalt with volatile petroleum diluent such as white spirits, kerosene or gas oil to render them more fluid for ease of handling and application. When the diluent evaporates, the initial properties of the asphalt are recovered. These products are used in spray applications as surface treatments and are handled at temperatures ranging from ambient to 300⁰F. However, air quality concerns have restricted their use.
- 3- Asphalt emulsions are fine dispersions of heated asphalt [base asphalt used in HMA applications] in water with an emulsifying agent. They are classified as cationic [electro-positively charged micells containing asphalt molecules], or anionic [electro-negatively charged micells containing asphalt molecules] depending on the emulsifying agent, and are graded according to chemical setting time. They can be applied as sprays or in cold mix applications for seal coating, maintenance and repair.
- 4- Mastic asphalt is a mixture of asphalt and fine mineral material in proportions so that it may be poured hot in place then compacted by hand troweling to a smooth surface for flooring, roofing and paving. It is not commonly used in the US.

Asphalt based Paints:

This product is a specialized cutback asphalt that can contain small amounts of other materials such as lampblack, aluminum flakes or mineral pigments. These paints are used as protective coatings in waterproofing operations and similar applications.

Specification Tests

Viscosity Test: Resistance to flow is measured at temperatures of 60⁰C (140⁰F), the maximum temperature of set asphalt pavement surfaces in US, and 135⁰C (275⁰F), the maximum mixing and lay-down temperature for hot asphalt pavements, using capillary or orifice-type viscometers.

Penetration Test: Indentation of an asphalt sample in tenths of a millimeter at 25⁰C is measured using a specified needle with a loading of 100g.

Softening Point test: Temperature is measured in ⁰C at which an asphalt, in the form of a disc under given loading conditions, softens and extends a fixed length.

Asphalt Workers

Approximately 3600 hot mix asphalt facilities and 7000 paving contractors employ nearly 300,000 workers in the US (data from Asphalt Paving Environmental Council, 1999 in NIOSH, 2000). Approximately 50,000 on-roof workers are exposed to asphalt fumes during, on average, 40% of their working hours, and 1500 to 2000 employees are exposed to asphalt fumes in approximately 100 roofing manufacturing plants (data from Asphalt Roofing Environmental Council, 1999 in NIOSH, 2000)

APPENDIX 4: Asphalt Carcinogenicity

Table A4.1 summarizes the carcinogenicity studies performed with asphalts and asphalt fumes. These include dermal mouse skin painting studies with whole bitumens of different grades, 2-year inhalation studies with asphalt fumes, and mouse skin painting studies with asphalt fume condensates.

Whole asphalts: Dermal exposure:

Undiluted penetration grade or oxidized asphalts, heated to make the materials mobile induced a few skin tumors (Simmers, 1965) but repeated burns caused by applying heated materials may have been responsible for cancer induction. Penetration asphalts diluted with organic solvents (acetone or benzene) produced an average tumor incidence of 2-2.7% indicating that whole asphalts had little or no carcinogenic activity. Skin painting of oxidized asphalts diluted with acetone, benzene or toluene gave more variable results, from essentially non-carcinogenic [0 or 2% tumor incidence] to weak [10% tumor incidence] (Hueper and Payne, 1960; Emmett et al., 1981). In a single study with 45% tumor incidence in which asphalt was diluted in toluene (Simmer, 1965), severe skin irritancy induced by the toluene vehicle may have exacerbated the asphalt effect. Skin effects from exposure of Swiss Albino mice to 8 different petroleum asphalts at concentrations of 25 μ l (10% in benzene), applied to the shaved backs twice a week for 81 weeks, included epidermal hyperplasia, inflammatory infiltration of the dermis, cutaneous ulceration and abscesses, and amyloidosis of the spleen and kidney. However only 6 of 218 mice (2.7%) exposed to any asphalt developed skin tumors (Wallcave et al., 1971) (IARC, 1985). Vacuum residuum samples (API 81-13, API 81-14) diluted in toluene, were applied to the shaved backs of C3H/HeJ male mice (100/group) at a concentration of 50 μ l, twice a week for approximately 130 weeks. After 12 months, 50 mice/group were terminated; no definitive systemic toxicity was observed although skin damage at the treatment site was evident (API, 1986). At the end of 130 weeks, API 81-13 had induced tumors in 5 mice with a mean latency period of 113 weeks, and API 81-14 induced tumors in 2 mice with a mean latency period of 120 weeks compared to a toluene control of 4 mice with tumors and a mean latency of 111 weeks. Neither vacuum residuum sample was carcinogenic in this assay (API, 1989a), nor did either sample act as a tumor initiator or promoter in a short-term initiation-promotion assay in CD-1 mice (API, 1989b). A two-year skin painting study of an AC-20 paving asphalt diluted in USP mineral oil and administered twice a week at concentrations of 37.5ml per application for 24 months, also did not show tumor induction in dermally treated mice (Exxon, 1991; McGowan et al., 1992). Overall, undiluted asphalts of any type are not carcinogenic by dermal exposure and dilution of asphalts with organic solvents may induce none to weak tumorigenesis over a long duration of treatment.

TABLE A4-1: Asphalt carcinogenicity studies

<u>MATERIAL TESTED</u>	<u>TREATMENT</u>	<u>DURATION</u>	<u>RESULTS</u>	<u>REFERENCE</u>
<u>Skin Application of Whole Asphalts</u>				
<u>Penetration asphalts</u>				
Steam refined (1 sample)	Undiluted (heated)	21 months	5/63 mice with skin tumors 21/63 mice survived study	Simmers (1965)
Road bitumen (4 samples)	Diluted with acetone (concentration unspecified) Application twice/week	2 years	0/100, 2/50, 1/50 & 0/50 mice with skin tumors	Hueper & Payne (1960)
Penetration bitumens (4 samples)	40% in benzene Application once/week	19 months	9/52, 4/47, 2/50 & 2/50 mice with skin tumors	Kireeva (1968)
Penetration bitumen (8 samples)	10% in benzene Application twice/week	>81 weeks	Highest incidence 7% Lowest incidence 0% Overall incidence 2.7%	Walrave et al (1971)
Penetration bitumen (1 sample)	30% in mineral oil Application twice/week	24 months	0/50 mice	McGowan et al (1992)
<u>Hard Asphalts</u>				
Bitumen paint (1 sample)	60% bitumen in mineral spirit Application once/week	30 weeks	1/40 mice with skin tumor	Robinson et al (1984)
<u>Oxidized bitumens</u>				
Air blown bitumen (1 Sample)	Undiluted (heated) Application 1 to 3 times/week	21 months	1/50 mice with skin tumor 10 mice survived	
Air blown bitumen (1 Sample)	90% in toluene Application three times/week	2 Years	9/20 mice with skin tumors	Simmers (1965)
Roofing bitumen (1 Sample)	Diluted in acetone, concentration unspecified Application twice/week	2 Years	1/50 mice with skin tumors	Hueper & Payne (1960)
Roofing bitumen (1 sample)	50% in toluene Application twice/week	80 weeks	0/50 mice with skin tumors	Emmet et al (1981)
Roofing bitumen (1 sample)	50% in acetone/cyclohexane Application twice/week	2 Years	3/30 mice with skin tumors	Sivak et al (1989)
<u>Mixed Penetration & Oxidized Bitumens</u>				
Mixture of 6 air-blown and steam-refined bitumens	Diluted with benzene, concentration unspecified Application twice/week	Time unspecified, but > 54 weeks	17/68 mice with skin tumors	Simmers et al (1959)
<u>Thermally cracked Bitumens</u>				
Oxidized residue bitumen (2 samples)	40% in benzene Application once weekly	19 months	9/49 & 4/42 with skin tumors	Kireeva (1968)
Vacuum residuum				
2 samples API 81-13 & 81-14	Diluted in toluene 50µl twice/week	130 weeks	5/50 & 2/50 mice with skin tumors Mean latency 113 & 120 wks	API (1989)

<u>Inhalation Carcinogenicity Studies</u>				
Oxidized bitumen (1 sample)	Fumes generated at 250-275°F Exposure 5 hr/day, 4 days/week 65 Bethesda strain rats 13 Guinea pigs used	2 Years	No lung tumors, but extensive fibrosing pneumonitis was observed in rats	Hueper & Payne (1960)
Mixture of 6 penetration grades and oxidized bitumens	20 C57 mice exposed 30 mins/day, five days/week Aerosol generated at 250°F	17 months	1 animal with lung adenoma	Simmers (1964)
Mixture of 6 penetration grades and oxidized bitumens	30 C57 mice exposed 6- 7½hrs/day five days/week Smoke generated at 250°F	21 months	Bronchitis, loss of bronchial cilia, epithelial atrophy, necrosis, pneumonitis No lung tumors observed	Simmers (1964)
<u>Skin Application of Condensed Fumes</u>				
Type I & Type III asphalt	Fumes generated at 450 & 601°F Application twice/week as 50% solution in cyclohexane/acetone. Some animals also exposed to UV light CD 1 and C3H mice used	Up to 72 weeks	C3H more sensitive than CD- 1. Greater tumor response from fume generated at the higher temperature.	Niemeier et al (1988)
Type III asphalt	Fumes generated same method as by Niemeier but at 601°F only C3H and Sencar mice used Sample applied twice weekly	104 weeks	C3H mouse 20/30 mice with tumors Sencar : 14/30 mice with tumors	Sivak et al (1989, 1997)

Asphalt fumes: Inhalation exposure

Two studies were performed in the 1960s; both investigators found evidence of non-specific respiratory irritation in some animals but no evidence of carcinogenicity. Hueper and Payne (1960) exposed Bethesda black rats or Strain-13 guinea pigs to fumes from a roofing asphalt (oxidized bitumen), 5 hr/day, 4 days/wk for 2 years. Fumes were generated by volatilizing air-blown asphalt from a dish heated to 120⁰-135⁰C (250⁰-275⁰F) inside the exposure chamber. None of the animals developed lung cancer but some rats or guinea pigs had chronic fibrosing pneumonitis with peribronchial adenomatosis. Simmer (1964) used a composite sample of asphalts (both steam and air-blown) from 6 different California refineries. The asphalt mixture was comprised of 32% asphaltenes, 32% resins, 14% saturates and 22% aromatics. C57 black mice were exposed to fumes from the pooled asphalt sample heated to 120⁰C (250⁰F) for 6-7.5hrs/day, 5 days/wk for 21 months. Histologic pulmonary changes included bronchitis, loss of bronchial cilia, epithelial atrophy and necrosis, and pneumonitis. No cancer was induced.

Asphalt Fumes: Dermal exposure

Fume condensates generated in the laboratory from Type 1 and Type III roofing asphalt at 232⁰C and 316⁰C (450⁰F and 601⁰F) were applied biweekly to the shaved backs of male CD-1

(nonpigmented) and C3H/HeJ (pigmented) mice (50mice/group) for 78 weeks; one half of each group was exposed to simulated sunlight (Niemeier et al, 1988). Asphalt samples were heated over time intervals of 4- 16.5 hours, in some cases repeatedly, to produce sufficient fume for testing. Tumors were induced by fume condensates from both types of asphalt; C3H mice demonstrated a greater response than CD-1 mice with a higher tumor incidence and shorter time-to-tumor latency period than CD-1 mice. The tumorigenic response of both types of asphalt was greater from fumes generated at 316^oC compared to fumes generated at 232^oC. Mean latency increased with simulated sunlight, which generally inhibited tumorigenic response. Sivak et al. (1989, 1997) heated Type III roofing asphalt from the same lot as Niemeier et al (1988) to 316^oC (601^oF), generated fumes, separated them into fractions A-E by HPLC, and analyzed fractions by GC/MS [Mutagenicity results for these fractions are discussed in the *in vitro* genetic toxicity section]. Raw roofing asphalt, neat asphalt fumes, asphalt residue after fumes were generated, reconstituted fumes and fume fractions individually or in various combinations were tested for carcinogenic and tumor-promoting activity in C3H/HeJ or Sencar mice (30 mice/group). Test material was applied twice a week for up to 104 weeks. Tumor-promotion was evaluated by a single treatment with B(a)P followed by individual application of fraction A (alkanes, alkylated benzenes, alkylated naphthalenes), D (alkylated phenols, alkylated ketones) or E (C6-C22 alkylated ketones, alkylated naphthols, and phenols), considered by the investigators as the fractions most likely to exhibit promoting or cocarcinogenic activity. Results indicated that raw roofing asphalt was only weakly carcinogenic (3/30 tumor bearing C3H mice), asphalt residue after fume generation was not carcinogenic, and neat asphalt fumes were dermally carcinogenic (20/30 C3H mice). Only fractions B and C which contained PAHs, S-PAC and O-PAC induced carcinomas (10/30 mice, 17/30 mice, respectively; other fractions (A, D, E) were not carcinogenic and did not act as tumor promoters or co-carcinogens in Sencar mice. Only combinations of fractions containing B or C induced carcinomas.

Although these skin-painting studies indicate that asphalt fumes generated under laboratory conditions produce skin tumors in mice, the compositional similarities between field-generated and laboratory-generated asphalt fumes have not been defined. In the NIOSH studies described above, asphalts were heated to higher temperatures for significantly longer periods of time than under field conditions, in order to generate sufficient fumes for testing. Thermal cracking, volatilization of constituents not released from asphalts under workplace conditions and other chemical reactions inconsistent with “real world” usage, make the results of these studies difficult to extrapolate to workplace hazard to man.

Fluorescence spectroscopy has also been used as a predictor of carcinogenicity for asphalt fumes. A method was developed that shows a high correlation between fluorescence emission intensity and carcinogenicity for 36 laboratory generated fume fractions, as measured in a mouse skin-painting bioassay (Osborn et al., 2001). Significantly, this method was then used to estimate the carcinogenic potential of U.S. paving worker samples. Emission levels, and therefore predicted carcinogenicity for these worker samples were at least 17-fold below the value that corresponds to a minimal carcinogenic effect, showing no measurable evidence of the cancer-causing components in the NIOSH rodent studies. (Kriech et al., 2002).