The Bitumen Industry—
A GLOBAL PERSPECTIVE

Production, chemistry, use, specification and occupational exposure

The Asphalt Institute is the international trade association of petroleum asphalt producers, manufacturers and affiliated businesses. Founded in 1919, the Asphalt Institute’s mission is to promote the use, benefits and quality performance of petroleum asphalt, through engineering, research, marketing and educational activities, and through the resolution of issues affecting the industry.

Eurobitume is the European industry association for the producers of refined bituminous products in Europe. The organisation was founded in 1969 and is based in Brussels, Belgium. Eurobitume is a non-profit organisation and works to promote the efficient, effective and safe use of bituminous binders in road, industrial and building applications.

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Asphalt Institute Inc. and European Bitumen Association—Eurobitume
Bitumen

1. Scope & terminology
This document concerns bitumen produced by petroleum (crude oil) refining. Although bitumen-like deposits also occur in natural asphalts, rock asphalts, lake asphalts and oil sands, the term “bitumen” in this document refers only to the product obtained from petroleum using various refining processes.

Petroleum bitumen is known by different names throughout the world. For example the terms “bitumen” and “asphaltic bitumen” are typically used in Europe and are synonymous with the term “asphalt”, or asphalt cement used in North America. Outside North America, the term “asphalt” is used to describe mixtures of bitumen with mineral materials. In this document the term bitumen will be used.

A glossary of terms appears at the end of this document (Appendix 1).

2. Introduction
Bitumen is an engineering material and is produced to meet a variety of specifications based upon physical properties. Bitumen is the residual product from distillation of crude oil in petroleum refining. This basic product is sometimes referred to as “straight run” bitumen and is characterised by CAS# 8052-42-4, or 64741-56-6 which also includes residues obtained by further separation in a deasphalting process. Bitumen can be further processed by blowing air through it at elevated temperatures to alter its physical properties for commercial applications. The general characteristics of oxidised bitumen are described by CAS# 64742-93-4. The vast majority of petroleum bitumens produced conform to the characteristics of these two materials as described in their corresponding CAS definitions.

Bitumen is produced to grade specification either directly by refining or by blending.

Bitumen should not be confused with coal derived products such as coal tar or coal-tar pitches. These are manufactured by the high-temperature pyrolysis (>800°C) of bituminous coals and differ from bitumen substantially in composition and physical characteristics. The differences between bitumen and coal-tar products are well defined in the literature.1, 2, 3

Similarly, bitumen should not be confused with petroleum pitches (CAS# 68187-58-6), which are often highly aromatic residues, produced by thermal cracking, coking or oxidation from selected petroleum fractions.1 The composition of petroleum pitches differs significantly from bitumen.

Bitumen also should not be confused with natural or lake asphalt such as Trinidad Lake Asphalt, Gilsonite, rock asphalt and Selenice. These products are unrefined and not produced by refining of crude oil. They often contain a high proportion of mineral matter (up to 37% by weight) and light components, leading to a higher loss of mass when heated.

A summary of CAS/EINECS numbers that have been used, or are available for use in bitumen production is given in Appendix 2.

2.1. Regional variations
In Europe, a survey of Eurobitume members for the seven countries in which a major epidemiology study4 was undertaken, showed that more than 95% of the bitumen produced in 2003 and 2004 corresponded to the two CAS numbers above, plus residues (petroleum), vacuum (CAS# 64741-56-6). A total of nine CAS numbers registered on EINECS cover refinery streams that may be used in bitumen manufacturing in Europe. The study further showed that less than 5% of petroleum bitumen produced corresponds to vacuum distilled thermal cracked residue (CAS# 92062-05-0), while the remaining 5 CAS numbers were either used only marginally or not reported to be used at all.
North American manufacturers of bitumen describe their products with two CAS numbers (Asphalt; CAS# 8052-42-4, and Asphalt, Oxidised; CAS# 64742-93-4). These, and four additional CAS numbers, have been introduced into a regulatory research programme being conducted by the US petroleum industry in cooperation with the US Environmental Protection Agency (EPA) as described below.

In 2003, the Petroleum ‘High Production Volume’ (HPV) Testing Group submitted to the US EPA its Test Plan for the Asphalt [bitumen] Category under provisions of the HPV Chemical Challenge Program. The additional category members are: Residues (petroleum) vacuum (CAS# 64741-56-6); Raffinates (petroleum) residual oil decarbonisation (CAS# 64742-07-0); Petroleum Resins (CAS# 64742-16-1) and Residues (petroleum) hydrodesulfurised vacuum (CAS# 64742-85-4). The vacuum residue substance (CAS# 64741-56-6) is analogous to straight run bitumen (CAS# 8052-42-4) (See Figure 2). The other category members are not considered “bitumen” but were included in the category because they consist primarily of high molecular weight hydrocarbons and have similar physical properties to bitumen. The extent to which any of these additional materials are used in commerce is not known.

In addition to these bitumen materials, the US EPA TSCA Chemical Inventory contains listings for a number of materials which are reaction products of asphalt or asphalt mixtures or both.

3. Production levels and uses

It is estimated that the current world use of bitumen is approximately 102 Million tonnes per year. Figure 1 shows estimated bitumen use and application by sector. The primary use of bitumen is for paving and roofing applications:

- 85% of all the bitumen is used as the binder in various kinds of asphalt pavements: pavements for roads, airports, parking lots, etc.
- About 10% of the bitumen is used for roofing. The rest of the bitumen, approximately 5% of the total, is used for a variety of purposes, each very small in volume. This sector is referred to as “Secondary Uses.”

Figure 1 - Global bitumen use and application areas

*Figures compiled in 2007 based on the most recent available data

4. Crude oil analysis and selection

Petroleum residues from the distillation of crude oils are the starting materials for bitumen production. Therefore the properties of the bitumen depend upon the properties of the residue from which the bitumen is manufactured. Of the multitude of crude oils commercially available, only a limited number are considered suitable for producing bitumen of the required quality in commercial quantities. In general heavy (Specific Gravity >0.9) crude oils are used to produce bitumen of the required quality. These types of crude oil tend to contain high sulphur contents (>1%m).
Bitumen residues, as a fraction of suitable crude oils, typically range between 20–50%m. In modern, integrated refineries a common practice is to blend multiple crude oils to produce consistent quality bitumen that meets the engineering specifications. Therefore the compositional analysis of bitumen produced by a given refinery will not vary greatly. Further, the nature of petroleum refining processes means that bitumens from different sources of supply are expected to be qualitatively similar.6

5. Bitumen manufacturing

Bitumen is a very complex combination of organic compounds containing a high proportion of hydrocarbons with high carbon numbers. This family of molecules can be found in many heavy crude oils. In its simplest form bitumen manufacturing separates the lighter fractions from the residuum, the required molecules being already present in the crude oil. For other types of bitumen, for example oxidised bitumens, the only way to achieve the desired properties is to produce new molecules through chemical reactions.

Several manufacturing methods are available to produce specification bitumens depending on the crude source(s) and processing capabilities available.7,8,9,10 Often a combination of processes is selected. The schematic in Figure 2 provides a compilation of refinery processes related to the production of bitumen.

Figure 2 - Schematic diagram of bitumen manufacturing

5.1. Distillation

The most common refining process used for producing bitumen is straight reduction to grade from petroleum crude oil or a crude blend, using atmospheric and vacuum distillation. In the schematic, atmospheric distillation is used to physically separate light, lower boiling point, petrochemical and fuel fractions from the non-boiling component known as atmospheric residue.

To remove the last traces of the lighter fractions, and avoid thermal transformation of the molecules, the atmospheric residue is introduced into a vacuum distillation unit. At reduced pressure it is possible to separate out any remaining lighter fractions, as the boiling temperatures are lower and unwanted thermal cracking of the molecules is avoided.

The lighter fractions, for example vacuum gas oils, are removed at atmospheric equivalent temperatures of 345–400°C (650–750°F) and 370–450°C (700–850°F) leaving a high boiling point hydrocarbon residue. The atmospheric equivalent temperature to yield the vacuum residue is up to 535°C (1000°F).
The residue from the vacuum distillation unit is used to manufacture bitumen. Depending upon the specification grade requirements the vacuum residue can be used either directly, further processed, or used as a component of blended bitumens.

The residual materials produced by distillation of atmospheric residue under vacuum are described by Asphalt (CAS# 8052-42-4) and Residues (petroleum) vacuum (CAS# 64741-56-6). In addition a further residual material (see section 5.4) is produced by vacuum distillation, but in this case the feedstock to the vacuum unit is derived from a thermal cracking rather than the atmospheric distillation unit.

5.2. Oxidation

Oxidised bitumen, also known commonly as blown bitumen, is made in a manufacturing unit known as the bitumen blowing unit (BBU) or Air Blowing Unit (ABU) or Oxidiser. Depending on the feedstock viscosity and the processing conditions, the BBU produces two types of product with distinctly different characteristics: air rectified (also known as semi-blown) and oxidised (also known as blown) bitumen. Both products are covered by the CAS# 64742-93-4.

The processes involve passing air through bitumen feedstock at elevated temperature in order to change the physical properties of the products. The main purpose is to harden the bitumen, increase its softening point and change the temperature-viscosity properties of the bitumen. The processes achieve this through varying degrees of chemical reactions which result in an increase in the average molecular weight of the bitumen leading to higher viscosity bitumen.

A mild degree of air blowing, known as air rectification, is commonly used to adjust the physical properties of a given feed in order to manufacture substances used to make products used in paving. Air rectified products are used at the same application temperatures as conventional vacuum distilled bitumens. Products that are air-rectified may be used in paving as well as some roofing applications, such as shingle saturants and Type 1 Built Up Roofing Asphalt (BURA), and also for some industrial applications.

An intense degree of air blowing, known as oxidation, is commonly used to adjust the physical properties of a given feed in order to manufacture substances used to make products for roofing, such as Type III BURA, and for some industrial applications. A Flux oil may be used to soften the feed to the BBU. A catalyst may also be used to increase the speed of reaction and improve temperature susceptibility relative to oxidation without a catalyst. Catalysts include such materials such as Ferric Chloride, Hydrochloric acid, Phosphorous Pentoxide, or Phosphoric acid.

The BBU consists primarily of a reactor, air blower, off-gas treatment facility, and temperature control equipment. The reactor is often an empty vessel, but may contain baffles or a mechanical agitation system to ensure turbulent mixing of the bitumen with air. The oxidation reaction is generally exothermic, therefore the reactor may be fitted with a water jacket, and/or a water spray facility at the head of the reactor to control the bitumen temperature. Injection of steam/water into the reactor head space may also be used to reduce the oxygen content of the off-gases, in order to manage the risk of fire or explosion. A schematic diagram of a bitumen blowing unit is provided in Figure 3.

Despite the complex reaction mechanisms and kinetics in the blowing unit, the general reaction pathway can be summarised as transformation of cyclic structures into resins (polar aromatics) which are, in turn, condensed to form asphaltenes (see section 7.1 for an explanation of these fractions). In bitumen blowing the primary oxidative process is carbon-carbon bond formation via oxidative condensation and to a lesser extent the formation of ester (and other oxygen containing) groups, both of which link smaller molecules into larger ones.

The chemical changes that take place during oxidation confer changes to the physical characteristics of the BBU feed that are dependent upon the severity of the oxidation process. As the reaction proceeds cyclics and resins that make up the oily maltene phase are converted into asphaltenes resulting in hardening of the bitumen (reduced penetration) and an increase in softening point. As the asphaltene concentration increases beyond a certain point, the ambient temperature flow properties of the bitumen change from visco-elastic to practically pure elastic behaviour. The severity of oxidation determines the temperature susceptibility of the product, with air rectified products (mild oxidation) having similar properties to those of straight run vacuum distilled (paving) bitumens. For this reason air rectified bitumens and vacuum distilled residues are used either directly, or in blends to produce finished products that have the same end use specifications. Oxidised bitumens have significantly different temperature susceptibility values as a consequence of their higher asphaltene contents and have a substantially higher softening points for a given penetration value. The combination of these properties cannot be obtained by simple distillation, or air rectification.
The rate at which the oxidation reaction occurs is affected by feedstock properties and the conditions in the blowing unit such as; viscosity or penetration of the feedstock, reactivity of the feedstock, temperature, air flow rate, degree of agitation, pressure, air to feed ratio, and whether or not a catalyst was employed.

Products from the air rectification and oxidation processes can be clearly differentiated using the characteristics such as;

- **Input Feed to Bitumen Blowing Unit**
  - Penetration
- **Change of properties: Input Feed versus Output Bitumen Blowing Unit**
  - Change in Softening Point
  - Ratio of Penetration (feed : output)
- **Output of Bitumen Blowing Unit**
  - Equiviscous temperature @ 0.1 Pa.s
  - Penetration Index
  - Softening point

**Figure 3 - Schematic diagram of the Bitumen blowing process**

* When used, typical flux oils include Heavy Vacuum Gas Oil and Re-refined Engine Oil Bottoms

### 5.3. Solvent deasphalting

The properties of the vacuum residue can be modified by use of subsequent refining process steps. Solvent deasphalting uses solvents to remove asphaltene fractions from distillation residues for the production of lubricating oil base stocks. The residue remaining after solvent deasphalting results in hard bitumens that can be used in blends to produce specification grade bitumens. The principal deasphalting processes use propane, butane, isobutene, pentane, or supercritical solvent extraction (ROSE process).

The residual products produced by processing through a solvent deasphalting unit are described by Asphalt (CAS# 8052-42-4), Asphaltenes (CAS# 91995-23-2) and Petroleum Resins (CAS# 64742-16-1) depending upon the process used.
5.4. Vacuum distillation of thermal cracked residue

In a visbreaking unit, a residue stream (either atmospheric, or vacuum residue) is heated to temperatures between 440–500°C (825–930°F), although process conditions can vary depending upon the feedstock and the desired properties of the thermally cracked material, to avoid coke formation. Long paraffinic side chains attached to aromatic rings are the primary cause of the high pour point and viscosity seen with residue streams. Visbreaking is carried out under conditions optimised to break off these long side chains and subsequently transform them to form shorter molecules with lower viscosity and pour point. It is believed that the process occurs via a free radical mechanism. The number of hydrogen atoms in the parent molecule is insufficient to provide the full compliment for each carbon atom and therefore unsaturated molecules are formed.\(^7,13\)

When used for bitumen production the thermally cracked residue is subjected to vacuum distillation to remove the distillate fractions which are then further treated and used in production of fuels. The product obtained after vacuum distillation is typically a hard material which can be used as a blending component for bitumen production.

The residual products produced by vacuum distillation of thermally cracked residue are described by Residues (petroleum), thermal cracked vacuum (CAS# 92062-05-0)

5.5. Other processes

A number of other refinery processes are used to produce small amounts of residual materials that can be used in the production of bitumen. These are primarily ‘further’ treatment or extraction processes applied to residual materials, to remove or convert constituents that are unsuitable for bitumen product performance and produce feedstocks for other processes. The processes, including solvent extraction, hydrodesulphurisation and hydrogenation, are not commonly used and hence represent only a minor part of the overall bitumen production.

6. Bitumen blending

The final bitumen product is produced to meet technical specifications, either directly in the refining process, or by blending of bitumens with different physical properties. Blending may take place at the refinery, at terminals, or at a third-party facility where blend components and finished products can be easily transported by truck, rail, or barge to their final locations. Higher viscosity products or bitumen may be blended with lower viscosity products or bitumen in suitable proportions to satisfy final product specification requirements. Bitumen specifications are covered in section 7.1.

6.1. Bitumen products

Bitumen is usually used without additives. However, it can be modified through the addition of non-bituminous components in order to provide a product with different physical properties required for its performance, or mode of application. Consequently the specifications for bitumen products are not necessarily the same as those for bitumen.

Examples of non-bitumen components used in bitumen products include:

- Adhesion agents (e.g. fatty amine derivatives, imidazolines)
- Crumb (scrap tyre) rubber
- Emulsifiers (e.g. fatty amine derivatives, tall oil soaps)
- Natural asphalts (e.g. Trinidad Lake Asphalt, Gilsonite)
- Petroleum distillates (e.g. Naphtha, white spirit, kerosene, gas oil)
- Polymers (e.g. Styrene-Butadiene rubbers, Atactic Polypropylene, Ethylene Vinyl Acetate, Ethylene Terpolymers)
- Polyphosphoric Acids
- Residues from the re-refining of waste engine oil (Refined Engine Oil Bottoms (REOB))
- Sulphur
- Waxes (e.g. Synthetic types such as Fischer-Tropsch and amide type waxes or natural waxes such as Montan wax)
- Bio binders (e.g. Vegetable based components)
- Warm Mix systems (e.g. Utilising surfactants or synthetic and natural waxes)
Manufacturers of bitumen products should identify any additives used in the product, in addition to any hazards or risks arising from the non-bituminous component(s). If appropriate, any risk transferred to the bitumen product should be identified. The non-bitumen blend components identified above are added at varying dosage levels depending on the additive.

Petroleum distillates can range from 5% to as much as 40% of the final blended material depending on the performance properties being targeted. According to Mundt, et al. petroleum distillates are the most widely used additive blended into bitumen for paving applications.

Crumb rubber, which has been used regionally for approximately 30 years, can range from as little as 5% to as much as 20% of the total binder weight, again depending on the properties being targeted. Within the past five years environmental efforts to eliminate stockpiles of discarded tyres have resulted in more widespread use of crumb rubber in bituminous blends.

Sulphur in some processes constitutes only a minor amount (<1%) to and is used to cross link styrene-butadiene polymers, but may comprise up to 40% by total binder weight when used to produce a sulphur extended asphalt. Concerns regarding evolution of H₂S and other sulphur compounds during initial construction and during recycling have slowed the adoption of sulphur as a bitumen additive.

Polymer additives generally range from 1% to typical levels of 3%, to as much as 7% for some applications.

Adhesion agents are generally utilized at levels below 1%, as are many of the warm mix systems based on additives blended into the bitumen.

If used, re-refined engine oil bottoms are typically present at 5% to 10% by weight of the binder. Localised use of REOB materials has been known for more than 20 years in the United States. In the past the main use for waste lubricating oils was as an industrial fuel. However, more recently economic incentives to re-refine waste drain oil to produce base oils have led to an increase in the volumes being re-refined. As a result there have been increased incentives to utilise these materials in bitumen. Little systematic research into the performance of pavements produced with REOB containing binders has been conducted. These materials can contain a number of contaminants introduced during the use of engine oils.

In the past other materials (such as light cycle oil, catalytically cracked clarified oil, coal tar derived material) have reportedly been blended with bitumen to produce bitumen products. A schematic diagram of the production routes for bitumen products is shown in Figure 4.

Most bitumen are supplied directly to a downstream user for processing and application as shown below. The two main application sectors are paving, accounting for approximately 85% of the total demand and roofing, accounting for approximately 10%. There are numerous other low volume applications in which bitumen is used, such as mastic asphalt, pipe coating, carpet backing, etc. In almost all applications bitumen is used in conjunction with other materials, e.g. hot mix asphalt comprises approximately 5%m bitumen, 95%m mineral aggregate. A schematic diagram of the bitumen supply chain is shown in Figure 5.

![Figure 4 - Schematic diagram of the manufacture of bitumen products](image-url)
Products which are mixtures of bitumen with non-bituminous components are beyond the scope of this document and will not be discussed in detail here. However, they include;

**Cutback and fluxed bitumens:**
These are products whose viscosity has been reduced (or “cutback”) by the addition of a volatile cut-back solvent, such as petroleum naphtha, white spirit (Stoddard solvent), kerosene, or gas oil. Fluxed bitumens generally use a relatively non-volatile solvent.

**Bitumen Emulsion:**
An emulsion in which the dispersed phase is bitumen or bituminous binder in water. The particle charge can be positive, negative, or uncharged depending upon the surfactant employed. The binder can be either a bitumen, a cutback, or modified bitumen.

**Modified Bitumen:**
A bituminous binder whose performance properties have been modified during manufacture by the use of one or more chemical agents such as polymers, crumb rubber, sulphur, or polyphosphoric acid.

Composition and potential exposure downstream of manufacturing operations is addressed in documents by application sectors for paving, roofing and mastic asphalt.15,16,17

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**Figure 5 - Schematic diagram of the bitumen supply chain**

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8
7. Physical properties and chemical composition of bitumens

At ambient temperature in-situ, bitumen is solid and virtually non-volatile. The vapour pressure of in-situ bitumen is below the limit of detection for normal instrumentation. Bitumen is normally heated to >140°C (284°F) to become liquid to facilitate transportation and handling. Typical physical properties are shown in Table 1. Some of these properties are regulated by national, or international specifications, while other properties, like specific gravity or vapour pressure, result from the manufacturing processes used to meet the performance specification.

Typical elemental analysis is given in Table 2. Bitumen contains predominantly cyclic hydrocarbons (aromatic and/or naphthenic) and a lesser quantity of saturated components which are mainly of very low chemical reactivity.

Table 1 - Typical physical properties for bitumen

<table>
<thead>
<tr>
<th>Property</th>
<th>Test Method</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flash Point, °C, Cleveland Open Cup</td>
<td>ASTM D92, EN 22592(b)</td>
<td>Varies according to grade; Typically &gt;230°C (445°F)*. &gt;270°C (520°F) in ASTM D312, &gt;250°C (482°F) in EN 13304</td>
</tr>
<tr>
<td>Loss on Heating, % (Maximum)</td>
<td>ASTM D2872, EN 12607-1</td>
<td>0.5-1% maximum depending upon the specification</td>
</tr>
<tr>
<td>Specific gravity value</td>
<td>ASTM D70, EN 15326</td>
<td>≥0.95, typically &gt;1.0, not a specification</td>
</tr>
<tr>
<td>Solubility, % (Minimum)</td>
<td>ASTM D2042, EN 12592</td>
<td>≥99% by specification (Trichloroethylene, Toluene, or Xylene as specified)</td>
</tr>
<tr>
<td>Solubility in water</td>
<td></td>
<td>Negligible</td>
</tr>
<tr>
<td>Softening Point</td>
<td>ASTM D36, EN 1427</td>
<td>&gt;30°C (86°F), grade dependent</td>
</tr>
<tr>
<td>Vapour Pressure</td>
<td></td>
<td>Below detection limit at ambient temperature</td>
</tr>
</tbody>
</table>

* Flash point varies with bitumen type. In some regions softer bitumens may have a significantly lower value

7.1. Bitumen and product specifications

Bitumen is available in a variety of grades. Specifications are tailored to meet the needs of the consuming industries and are based on a series of physical tests that define the safety, solubility, viscoelasticity, and durability of bitumen. These physical properties are designed to optimise performance under high and low temperature conditions.

In the following sections the U.S. and European specification systems are described in detail because it is believed that these two systems are comprehensive and represent worldwide principles. Specifications outside the U.S. and Europe are based on assessment of similar characteristics using similar test methods for high, low and intermediate service temperature properties and durability.

7.1.1. U.S.

A relatively new system, referred to as the Performance Graded (PG) system, is used to grade bitumen in the United States. The PG system was developed as part of the $150 million, 5-year Strategic Highway Research Program (SHRP) conducted from 1987 to 1992. The PG system has replaced the Penetration and Viscosity grading systems used in the past. The climatic conditions (primarily temperature) to which pavements are exposed are a key element of the PG system. For example, PG 64-22 bitumen is intended to provide enough stiffness at a 64°C pavement temperature, determined at a 25mm pavement depth, to help the mix resist permanent deformation or rutting; a low enough
stiffness at -22°C pavement temperature to prevent low temperature thermal cracking; and a low enough viscous modulus at intermediate temperatures to minimise fatigue cracking. Both conventional (unmodified bitumen) and polymer modified bitumens are accommodated under the PG system. The standard PG specifications are contained in AASHTO M320-04 and ASTM D6373 which also includes assessment of durability of bitumens and safety aspects (flash point and loss on heating). However, several states have modified these requirements based on their past experience with PG bitumens and/or bitumen supply considerations specific to their area. Most of the modifications to the PG grading system incorporate tests specifically designed to encourage suppliers to incorporate elastomeric polymer additives into the bitumens.

While oxidised bitumens (also known as air-blown) are graded on the basis of softening point, there are also penetration test requirements at three temperatures (0°C, 25°C, and 46°C) that provide some control over the temperature susceptibility of these materials. Required tests for specialised applications of oxidised bitumen can be found in "The Asphalt Handbook."²⁰

7.1.2. Europe

Bitumen Specifications in Europe are based upon broad categories of binder type shown in Figure 6 and include bitumen derivatives (preparations) in addition to pure bitumens. The system of harmonisation is based mainly upon physical properties rather than chemical type. The system of European harmonised specifications is administrated by the Comité Européen de Normalisation (CEN). The member states involved comprise the 27 members of EU plus 3 European Free Trade Agreement (EFTA) states (Norway, Iceland and Switzerland).

CEN TC336 Working Groups produce ‘harmonized’ specifications and test methods for bitumens.

7.1.2.1. Europe paving bitumen specifications

Nomenclature and grading in Europe is based on the penetration range of the product [a measure of consistency at 25°C (77°F)]. Paving bitumen specifications include EN12591 (paving grades), EN13924 (hard grade paving bitumens) and EN14023 (Polymer Modified Bitumens), the latter specification being bitumen products comprising bitumen plus other materials including polymers. These are based on the various existing (empirical) test methods and former national standards, which were in common use for many years.

The specified properties relate to rheology (penetration, softening point, viscosity), resistance to hardening/ageing, flash point (for safety reasons) and solubility to indicate absence of contaminants. Paving grade bitumens are produced by vacuum distillation and air-rectification. Polymer modified bitumens, which are blends of bitumen with polymers and other additives, are also categorised as paving bitumens.

7.1.2.2. Europe industrial bitumen specifications

For industrial bitumens the European Standards provide a framework for the specification of oxidised or hard industrial bitumen, used mainly in roofing, waterproofing and adhesives. These bitumens are covered by EN13304 (Oxidised bitumens) and EN13305 (Hard Industrial Grade bitumens).

Within Europe several grades of oxidised bitumens are used and, dependent on climatic conditions, type of building construction and traditional practices, different grades may be used for the same purpose. However, the bitumen grades used are produced to withstand significant diurnal and seasonal temperature variations and are therefore manufactured by severe blowing in order to reduce their temperature susceptibility in comparison to paving bitumens. This reduced sensitivity to temperature is reflected in the specifications.

Oxidised bitumens are graded by a combination of the values of softening point and penetration at 25°C, expressed as multiples of 5. Rather than setting out a specification with defined acceptance limits, the framework specifies mandatory, optional and informative tests to be carried out on bitumens. The framework in the European standard for oxidised bitumens (EN13304) provides a basis for quality agreements to be established between supplier and client. Typical grades of oxidised bitumen are: 85/25, 85/40, 95/25, 95/35, 100/40, 105/35, 110/30, 115/15.
Hard industrial bitumens are used mainly in flooring, varnishes, mineral rubber, roofing and mastic asphalt. Within Europe several types of hard industrial bitumen are used, and dependent upon traditional practices, different grades may be used for the same purpose. As with oxidised bitumens, there is a framework standard for hard industrial grades. The framework in the European standard for these products provides a basis for quality agreements to be established between supplier and client, rather than identifying specific grades.

Hard industrial bitumens are graded by the specification limits for softening point values, expressed as multiples of 5, and are characterised by an H in front of the values. The specification system for the hard industrial grades (EN13305) does not differ significantly in the types of testing required. Typical grades for hard industrial bitumen are: H80/90, H85/95, H90/100, H100/110, H155/165.

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**Figure 6 - European bituminous binder specification structure**

7.2. Types and structures of functional groups

The chemical composition of bitumens is generally similar, but with some variation depending upon the original crude oil and on the processes used during refining and blending. Bitumens can generally be described as complex mixtures containing a large number of different chemical compounds of relatively high molecular weight. There is considerable uncertainty as to the molecular weight distribution of bitumen. The smallest size, approximately 300, is determined by the distillation ‘cut point’ during the manufacture of the bitumen. The largest size has not been finally concluded; earlier research suggested that molecular weights up to 10000 are present\(^\text{21}\), while some recent research\(^\text{22}\) indicates that there are probably very few, if any, molecules larger than 1000 in bitumen.

The molecules present in bitumens are combinations of alkanes, cycloalkanes, aromatics and hetero-molecules containing sulphur, oxygen, nitrogen and heavy metals.\(^\text{23}\) The hetero-atoms, sulphur, nitrogen and oxygen, are typically found in the asphaltene and resin components.

Bitumen functionality relates to how molecules interact with each other and/or with aggregate surfaces and/or other materials. The content of nitrogen and oxygen in some molecules makes them slightly polar, but the limited amount of nitrogen and oxygen prevents the existence of very polar molecules. The significance of molecules containing hetero-atoms in bitumen chemistry is the ability to form molecular associations, which strongly influence the physical
properties and performance of bitumens. The resin and asphaltene components containing the hetero-atomic compounds can vary in content and characteristics in bitumens obtained from different crude sources. The predominant sulphur compounds are thiophenes, and the predominant nitrogen compounds are based on pyrrole, indole, and carbazole groups. Predominant oxygen compounds appear to include furans, phenols, and carboxylic/naphthenic acid groups.

Table 2 - Elemental analysis of bitumens from various sources

<table>
<thead>
<tr>
<th>Element</th>
<th>Range</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon, %w</td>
<td>80.2 - 84.3</td>
<td>82.8</td>
</tr>
<tr>
<td>Hydrogen, %w</td>
<td>9.8 - 10.8</td>
<td>10.2</td>
</tr>
<tr>
<td>Nitrogen, %w</td>
<td>0.2 - 1.2</td>
<td>0.7</td>
</tr>
<tr>
<td>Sulphur, %w</td>
<td>0.9 - 6.6</td>
<td>3.8</td>
</tr>
<tr>
<td>Oxygen, %w</td>
<td>0.4 - 1.0</td>
<td>0.7</td>
</tr>
<tr>
<td>Nickel, ppm</td>
<td>10 - 139</td>
<td>83</td>
</tr>
<tr>
<td>Vanadium, ppm</td>
<td>7 - 1590</td>
<td>254</td>
</tr>
<tr>
<td>Iron, ppm</td>
<td>5 - 147</td>
<td>67</td>
</tr>
<tr>
<td>Manganese, ppm</td>
<td>0.1 - 3.7</td>
<td>1.1</td>
</tr>
<tr>
<td>Calcium, ppm</td>
<td>1 - 335</td>
<td>118</td>
</tr>
<tr>
<td>Magnesium, ppm</td>
<td>1 - 134</td>
<td>26</td>
</tr>
<tr>
<td>Sodium, ppm</td>
<td>6 - 159</td>
<td>63</td>
</tr>
</tbody>
</table>

The chemical characterisation of bitumens is based on their separation into four broad classes of compounds - asphaltenes, saturates, cyclics and resins - using solvent precipitation and adsorption chromatography (ASTM D4124-01 Standard Test Methods for Separation of Asphalt into Four Fractions). The relative content of these groups of compounds varies. Examples of the typical structures of the fractions are given in figure 7.

Asphaltenes are black amorphous solids containing, in addition to carbon and hydrogen, some nitrogen, sulphur and oxygen. Trace elements such as nickel and vanadium are also present. Asphaltenes are generally considered as highly polar aromatic materials of high molecular weight and constitute 5–31% of the mass of bitumens.

Saturates comprise predominantly the straight and branched-chain aliphatic hydrocarbons present in bitumens, together with alkyl naphthenes and some alkyl aromatics. The average molecular weight range is approximately similar to that of the cyclics, and the components include both waxy and non-waxy saturates. This fraction forms 5–20% of the mass of bitumens.

Cyclics (Aromatics/naphthene aromatics) comprise the compounds of lowest molecular weight in bitumens and represent the major proportion of the dispersion medium for the peptised asphaltenes. They constitute 30–60% by mass of the total bitumen and are dark viscous liquids. They are compounds with aromatic and naphthenic nuclei with side chain constituents and have molecular weights of 500–900 (number average).

Resins (polar aromatics) are dark-coloured, solid or semi-solid, very adhesive fractions of relatively high molecular weight present in the maltenes. They are dispersing agents (referred to as peptisers) for the asphaltenes, and the proportion of resins to asphaltenes to a degree governs the rheological behaviour of bitumens. Resins separated from bitumens are found to have molecular weights of 800–2000 (number average) but there is a wide molecular distribution. This component constitutes 15–55% of the mass of bitumens.

Vacuum distillation selectively removes higher volatility, lower molecular weight hydrocarbons, thereby resulting in a concentration of higher molecular weight (lower volatility) components in bitumen. During air-blowing, cyclic
compounds are converted to resins, which are in turn converted to asphaltenes. As the asphaltene content increases the stiffness of the bitumen increases. Oxidised bitumens typically have higher asphaltene contents than those of non-oxidised grades.

Chemical changes in the bitumen on blowing are covered in detail in section 5.2.

The relative inertness of bitumen makes it particularly suitable for use in durable construction products, such as road pavements and waterproofing applications. Under ambient conditions the physico-chemical properties change very slowly over the service life, which is typically decades. The fact that in-situ bitumen hardens slowly over the service life is reported to be due to the formation of additional asphaltenes by oxidation.

![Figure 7 - Example of the broad chemical types present in bitumen](image)

Attention has already been drawn to the presence of minor amounts of sulphur, oxygen and nitrogen in bitumen. The sulphur content may be 1–7% by mass in common products and can consist of many different sulphur compounds. Studies of the rate of oxidation reactions have shown that the hetero-atoms, sulphur, oxygen and nitrogen, occur largely in stable configurations, probably rings. X-ray diffraction points to the presence of naphthenic groups as well as aromatic and paraffinic groups. Other work led to the conclusion that oxygen and nitrogen as well as vanadium (80–4300 µg/g) and/or nickel (<100 µg/g) are combined in some form in asphaltene structures. It has been proposed that the metals are chemically associated with the ‘asphaltic material’ (asphaltenes), the sites being holes in the aromatic clusters, which are edged with the sulphur, oxygen and nitrogen atoms.

7.3. Polynuclear Aromatic Hydrocarbons

Crude oils contain traces of polynuclear aromatic hydrocarbons (PAHs), which partly end up in bitumen at ppm levels. The maximum temperatures involved in the production of bitumen, ranging from 350–500°C (660–930°F), are not high enough to initiate significant PAH formation, which requires pyrolysis or combustion and typically takes place at temperatures above 500°C (930°F). The principal refinery process used for the manufacture of bitumens,
vacuum distillation, is effective at removing polycyclic aromatic hydrocarbons (PACs), including PAHs with 3–6 unsubstituted, fused rings. At elevated temperatures, the small amounts of 3-6 ring PAHs remaining in the residue are found in the aerosol fraction of the fumes (see section 8). The levels of PAHs analysed in various bitumens and bitumen fumes are shown in Table 3.

### Table 3 - PAH content of bitumen and bitumen fumes

<table>
<thead>
<tr>
<th>PAH</th>
<th>PAH in Bitumen</th>
<th>PAH in bitumen fumes (personal samples*)</th>
<th>µg/m³</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/kg (ppmw)</td>
<td>(personalsamples*)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>2.5 - 3.0</td>
<td>5.5 (8/9)**</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>BDL - 0.7</td>
<td>3.3 (1/9)</td>
<td>7.8</td>
<td></td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>NR</td>
<td>3.3 (2/9)</td>
<td>8.5</td>
<td></td>
</tr>
<tr>
<td>Fluorene</td>
<td>0.3 - 0.5</td>
<td>0.47 (1/9)</td>
<td>0.84</td>
<td></td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>0.3 - 7.3</td>
<td>0.82 (2/9)</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>Anthracene</td>
<td>BDL - 2.0</td>
<td>0.063 (1/9)</td>
<td>0.074</td>
<td></td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>BDL - 2.0</td>
<td>0.98 (1/9)</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>Pyrene</td>
<td>0.2 - 8.3</td>
<td>NA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chrysene</td>
<td>&lt;0.1 – 11</td>
<td>NA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzo(a)anthracene</td>
<td>BDL - 3.3</td>
<td>NR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perylene</td>
<td>BDL – 39</td>
<td>NR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzofluoranthenes</td>
<td>BDL - 1.2</td>
<td>0.65 (1/9)</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>Benzo(e)pyrene</td>
<td>&lt;0.1 - 13</td>
<td>0.78 (1/9)</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>BDL - 4.6</td>
<td>0.16 (1/44)</td>
<td>0.072</td>
<td></td>
</tr>
<tr>
<td>Dibenzanthracenes</td>
<td>BDL - 3.3</td>
<td>NR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Indeno(1,2,3-cd)pyrene</td>
<td>BDL - 2.4</td>
<td>NR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzo(ghi)perylene</td>
<td>&lt;0.1 - 4.6</td>
<td>NR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthanthrene</td>
<td>BDL - 0.1</td>
<td>NR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dibenz(a)anthracene</td>
<td>BDL - &lt;0.6</td>
<td>NR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dibenz(a)pyrene</td>
<td>BDL - &lt;0.6</td>
<td>NR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coronene</td>
<td>BDL - 1.9</td>
<td>NR</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Personal exposure monitoring at terminals and refineries
** Results represent arithmetic mean of samples; (numbers in parentheses indicate numbers of samples above the limit of detection/number of samples)
NA = Not Applicable
NR = Not Reported
BDL = Below Detection Limit
Note: data on PAH content of bitumen and those for PAH in fumes are from different studies. See references for further details.
8. Bitumen fume defined

Due to the manufacturing process, which removes the lower boiling point molecules, bitumens do not emit fumes under normal conditions of service.

Bitumen fume is the “term of art” used to describe the emissions from heated bitumen and products containing bitumen. The system is in a dynamic equilibrium as illustrated in Figure 8. Traditionally bitumen fume is the material which is measured and reported to reflect the level of potential occupational exposure.

During handling of bitumen, or bitumen-containing materials at elevated temperatures, small quantities of hydrocarbon emission are evolved. In a laboratory study, in the temperature range relevant for paving applications (140–190°C (285–375°F)), the emission rate of the Benzene Soluble particulate matter increases by a factor of 2 for about every 11–12.5°C (20–22°F) temperature increase. In the temperature range relevant for roofing applications (210–270°C (410–520°F)) it is a factor of 2 for every 14–17°C (25–30°F). Occupational exposure to bitumen fume is often characterised by measurement of the aerosol fraction containing 3-6 ring PAH compounds. At operating temperatures below 140°C the boiling range of emissions is such that there is no significant exposure to such aerosols and exposure is predominantly to bitumen vapour.

Numerous sampling and analytical methods have been, and continue to be, employed in the characterisation of workplace exposure. Different methods can measure different fractions of the fume. As a result reported values of potential exposures over time and between studies must be considered carefully before drawing conclusions on dose-response relationships or potential risk estimates.

Different methods for sampling personal exposure, or atmosphere composition exist and they have differing collection efficiencies for the various fractions contained in bitumen fumes. The full extent of relationships between the various methods remains unknown; this leads to difficulty in comparing results from different studies.

Gas molecules and bitumen droplets are typically a minor proportion of the emissions from hot bitumen. The ratio of aerosol/mist to vapour will vary with ambient and operating conditions. Typically the aerosol: vapour ratio is in the range 5:95 – 15:85, but it needs to be recognized that under certain conditions, such as high temperature, the actual ratio may vary outside this range.

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**Figure 8 - Schematic diagram of bitumen fume**
Workplace exposure measurements may capture particulate matter which is dispersed in air. In specific applications, e.g. roofing tear-off or pavement milling, this may include solid bituminous material as a result of mechanical agitation or attrition, or by removal of old bitumen containing material, such as asphalt pavement, or bitumen roofing materials.

Exposure measurements are susceptible to distortion in magnitude and composition due to the influence of potential confounders that can interfere with standard sampling and analytical techniques. Potential confounders which may exist in the ambient environment include mineral dust, exhaust particulate and hydrocarbon vapour from diesel/gasoline emissions and cigarette smoke. Other confounders include materials added post refining (e.g. diluents, anti-strip, polymers, fibres, mineral fillers, natural bitumens, sulphur used for cross-linking polymer, crumb rubber etc.) which may be introduced through the use of different application technologies.

Bitumen fume is a complex mixture having a broad boiling point range. The molecular composition can include hydrocarbons covering the range from naphtha through to long branched chain aliphatic hydrocarbons, cycloalkanes, aromatics and hetero-molecules containing sulphur, oxygen, occasionally nitrogen, and low levels of polynuclear aromatic compounds (PAC), including PAH.

Laboratory studies on bitumen fumes often require significant quantities of sample which cannot be obtained easily from field activities. The low level of emission in many applications means that prolonged sampling periods are needed to collect sufficient fume for reliable measurement. Surrogate materials can be generated using laboratory methods which are representative of fumes to which workers are exposed. Such material is normally collected as a condensate, combining aerosol, vapours and gaseous fractions. Accordingly, any artificially generated fume condensate must be characterized and matched against fumes found in the workplace.

9. Occupational exposure monitoring of bitumen fumes

Occupational exposure to hot bitumen can lead to thermal burns, therefore personal protective equipment is normally used to prevent skin contact. When bitumen is cold it becomes solid, or semi-solid, therefore there is no personal exposure unless dust particles are generated, e.g. during removal of old material containing bitumen.

When bitumen is heated small quantities of hydrocarbon vapours and gases and sometimes inorganic gases (e.g. H₂S) are emitted. Some of the heavier molecules in the vapour will condense on nuclei and form droplets (aerosol phase). At workplaces, the size distribution and the partitioning between gas, vapour and aerosol phase is strongly dependent on environmental conditions. At different bitumen fume concentrations, caused e.g. by type of bitumen used, application temperature, changing wind speeds or convective flows and distance from source, the ratio of aerosol to vapour phase can be quite different.39,37 The particle (droplet) size distribution of the aerosol phase might also change considerably.38

Most of the aerosol evolved from the bitumen is expected to be in the respirable size range, although inorganic particulates from non-bitumen sources can be outside this range.40 Numerous sampling and analytical methods have been and continue to be employed in the characterisation of workplace exposures to bitumen fume and the full extent of any relationships between these various methods remains unknown. Additionally bitumen fume, vapour and PAH have different determinants of exposure. In an analysis of paving worker exposures in Denmark, Finland, France, Germany, Norway, and Sweden, no correlation between bitumen aerosol and bitumen vapour levels could be established.41 The same study identified a significant reduction in worker exposure to bitumen fumes over the last 50 years.
9.1. Exposure limits

It is desirable that occupational exposure to bitumen fume is measured using a personal monitoring sampler. Collection of static, or environmental samples does not necessarily provide a reliable indication of personal exposure. The type of sampler used and the method by which it is analysed can lead to substantial differences between measured values.\textsuperscript{42} When comparing results of personal exposure monitoring surveys it is important to take into account the method used and the metric being employed. Exposure monitoring methods for bitumen fume fall into three main categories that measure:

**Particulate matter**

TPM (Total Particulate Matter): this includes aerosol matter from the bitumen and inorganic material such as dust, rock fines, filler etc. Because TPM methods collect material from non-bitumen sources the resulting values can suggest artificially high exposure values, especially in dusty environments.

**Solvent soluble fraction of particulate matter**

BSM/BSF (Benzene Soluble Matter/Fraction) or CSM/CSF (Cyclohexane Soluble Matter/Fraction): these methods rely on collection of the particulate fraction as described above. However, in order to reduce the confounding exposure to inorganic particulate matter a solvent is used to extract only the organic fraction of the particulates. Such methods more accurately define the exposure to the agent of interest (bitumen fume).

A sub-set of such methods uses a special monitoring cassette to collect only a specific fraction of the particulate matter, e.g. the respirable, thoracic or inhalable fractions.\textsuperscript{43}

**Organic matter**

TOM/THC (Total Organic Matter/Total Hydrocarbon): the sum of the organic part of the particulate fraction plus the organic vapour phase collected using a back-up absorbent.

For each of the above categories there are numerous variables, such as type of sampler (e.g. open face, closed face, inhalable particulate), the type of solvent used to extract the filter (e.g. cyclohexane, benzene, dichloromethane), the type and quantity of sorbent used to capture the vapour phase (XAD 2, Tenax\textsuperscript{TM}, activated, or coconut charcoal), analytical method and flow rate of air through the filter, which may influence the measured values. The resulting differences make it difficult, if not impossible, to directly compare measurements taken using different methods.\textsuperscript{44,45}

At present, no international standardised method for sampling and measuring potential bitumen fume exposure exists, but occupational exposure limits for bitumen fumes have been set in over 50 countries, Canadian provinces and U.S. states. Regulatory limits in different countries and voluntary guidelines developed by independent authorities vary considerably in respect of numerical values and methods of evaluation. More than half use an 8-hour time-weight average (TWA) concentration of 5 mg/m\textsuperscript{3} (typically as total particulate matter). Slightly less than half set the TWA at 0.5 mg/m\textsuperscript{3}, which usually measures just the inhalable fraction of benzene soluble extracts of the aerosolized fume. Switzerland uses a limit of 10 mg/m\textsuperscript{3} total aerosol and vapor, and Slovenia sets a limit of 10 ml/m\textsuperscript{3}, which measures aerosol and vapour from warm processing. Ten countries have set short term exposure limits (a TWA exposure not to be exceeded in any 15-minute interval) of 10 mg/m\textsuperscript{3} fume (typically total aerosol and vapour).

Ceiling limits (a concentration which should not be exceeded during any part of the workshift) of between 1.5 and 12.5 mg/m\textsuperscript{3} total fume are in place in three countries.

In the U.S., there is no federal Occupational Exposure Limit (OEL) for asphalt fume, however NIOSH recommends a 15 minute ceiling limit of 5 mg/m\textsuperscript{3} measured as total particulate matter. The American Conference of Governmental Industrial Hygienists (ACGIH\textsuperscript{®}) a professional society which issues proprietary guidelines has issued a Threshold Limit Value (TLV\textsuperscript{®}) for asphalt (bitumen) fume of 0.5 mg/m\textsuperscript{3} Time Weighted Average (TWA)\textsuperscript{47} as benzene soluble aerosol (portion of the) inhalable fraction, a recommendation widely adopted by many countries.

Bitumen fume-induced upper respiratory tract and eye irritation are the health-based endpoints used typically to establish workplace limit values for asphalt (fume), while cautionary statements concerning potential cancer hazard and/or absorption through the skin are often included as part of the criteria. Further research into potential health effects and, if documented, their underlying causation will be required to reach consensus on a standardised occupational exposure limit (OEL) and a suitable metric; this may be followed by further development of appropriate sampling techniques and analytical methods.

It should be recognised that none of the methods of measuring exposure are bitumen specific and will capture particulate and vapour fractions of any organic material. Therefore exposure levels can be subject to confounding from other organic materials in the workplace, such as solvents used for cleaning and diesel engine exhaust.
In addition to monitoring exposure to bitumen fumes some studies have evaluated exposure to individual, or groups of Polynuclear Aromatic Hydrocarbons (PAH) as components of bitumen fumes. A number of different lists of PAHs are used because different researchers, regulators and advisory bodies have their own view of which substances should be regarded as potentially hazardous.

9.2. Dermal

At ambient temperature bitumens are solid, or semi-solid materials. Apart from physical abrasion, skin contact with solid bitumen is not expected to cause health effects. The high temperatures required to handle and apply bitumen can result in serious thermal burns if contact occurs and consequently skin contact with hot product is unlikely, except in accident situations. However, some bitumen preparations, in particular those containing diluents to reduce the viscosity of the mixture, are handled and applied at low, or ambient temperature where skin contact may occur.

Traditionally, exposure monitoring has focused on inhalation as the primary route of exposure. However, in recent years the possibility of dermal exposure and uptake of components of bitumen fumes, arising from dermal contact with condensed fumes/emissions has been considered. This section covers studies of dermal exposure to bitumen fume. Other documents 15,16,17 detail exposure to bitumen during handling and application of materials containing bitumen during use in paving, roofing and mastic asphalt operations.

There are few published data available on occupational dermal exposure and uptake for neat bitumen. However, some laboratory work on dermal transfer of dimethyl sulphonyl (DMSO) extracts from a range of oil products 48 and radiolabelled benzo(a)pyrene (BaP) mixed with oil products was carried out on a range of products including bitumen. 49,50 A related study looked at dermal transfer of radiolabelled BaP using two different carrier liquids. 51 The studies conclude that dermal uptake of PAH from bitumen, or preparations containing bitumen, are extremely low and influenced mainly by product viscosity and the type of diluent (solvent) employed in the preparation.

As part of a multi-country, nested case control study on lung cancer risk among asphalt workers, 52 Bofetta et al included an assessment of dermal exposure to bitumen fume condensate, using the DREAM methodology. 53 This visual observation method provides a task based, semi-quantitative estimate of dermal exposure; trained occupational hygiene observers used a structured approach to estimate type, body site, duration and magnitude of dermal contact, taking into account the dermal protection afforded by clothing and personal protective equipment. Estimates were validated by comparison to measured data on dermal exposure in the published literature. Results confirmed that rakers and screedmen showed the highest level of dermal exposure during road paving operations. The main skin site exposed was the hands, with direct transfer and deposition being the dominant routes of exposure. No relationship was found between dermal exposure to fume condensate and lung cancer incidence.

Skin exposure to speciated PAH compounds has been a component of several exposure assessments. One of these examined workers in the U.S. employing techniques which were considered standard at the time of the study. Briefly the sampling and analytical procedure consisted of collection of dermal wipe samples taken from the back of the hand and/or forehead of workers. Smear tabs, premoistened with isopropyl alcohol, were used to wipe a 4 by 8 cm skin area followed by extraction of the benzene soluble fraction and subsequent analyses for 6 marker PAHs identified in OSHA method 58. 54 The remaining 26 samples were analysed for all 17 PAH species in NIOSH Method 5506. 55 Six of the 17 PAH species were detected in one or more samples: Chrysene, Dibenzo(a,h)anthracene, Fluoranthene, Naphthalene, Indeno(1,2,3-cd)pyrene and Phenanthrene. The majority of the 131 samples collected were reported to yield below detectable results for all analytes. In the refinery terminals sector of this study only two wipe samples provided values above detectable limits, both of these for naphthalene. Additional detail is contained in reference 35.

Biological markers (biomarkers) have been used to assess exposure to PAHs during occupational exposure to bitumen fume. 1-hydroxy-pyrene in urine is a widely used biomarker for monitoring exposure to pyrene.

In a study with volunteers exposed to bitumen fume in an exposure chamber, Knecht et al. measured dermal uptake by monitoring urinary PAH-metabolites in volunteers exposed with and without a fresh air supplied respirator. Urinary hydroxy-pyrene, hydroxy-chrysene and hydroxy-phenanthrene were used as indicators of total absorbed dose. Based on this controlled laboratory experiment, it was concluded that the contribution of dose via the respiratory and dermal routes were approximately equal with 57% of the dose of pyrene and chrysene being absorbed through the skin and 50% of the phenanthrene absorbed by that route. 56
These studies and others are described in more detail by van Rooij et al. in “Review of Skin Permeation Hazards of Bitumen Fumes.” The authors concluded that “the methods for the determination of the actual dose rate due to dermal exposure of workers are not yet validated. Aspects such as (i) transfer rate to the pseudo skin pads or patches compared to real skin transfer are not known, (ii) the estimation of the total body dose is not standardised, (iii) data on permeation coefficients of carcinogenic compounds through human and animal skin are limited, and (iv) it is not known which part of the 8-hour contamination on workers skin becomes available in target tissues.”

9.2.1. Laboratory methods for assessing dermal uptake

A laboratory study to evaluate the rate of dermal uptake of certain components of bitumen fume condensate was carried out. Nonviable human cadaver skin was mounted in Franz diffusion cells and bitumen fume condensate was applied at infinite dose. Flux rates of anthracene, fluoranthene/pyrene and total 3–6 ring PACs were determined by HPLC fluorescence detection. Results indicated that, under in vitro infinite dose conditions, skin penetration of PAC was not detectable before 3 hours.

9.3. Refinery and terminal exposure data

Workplace exposure measurements are susceptible to variability, in magnitude and constituent, from a variety of potential confounders, some of which may be introduced in the manufacturing process, others through application technologies and others which may pre-exist in the ambient environment. As a result, reported values of exposures over time, between studies, and between the various countries must be considered carefully before use in development of dose-response relationships or potential risk estimates.

A summary of refinery and terminal exposure data is given in Appendix 3. Exposure data during handling and application of bituminous materials can be found in other documents devoted to the specific sectors paving, roofing and mastic asphalt.

9.4. Further reading on occupational exposure


Cancer Mortality Among European Asphalt Workers: Selected papers from a study of cancer risk in the European asphalt industry coordinated by the International Agency for Research on Cancer; American Journal of Industrial Medicine, Vol 43, 1, 2003


10. Aqueous emissions (leaching)

Bitumen is a very inert material that is insoluble in water. Kriech examined six paving and four roofing bitumen samples to determine the concentration of 29 PACs in leachate waters under laboratory conditions. The majority of results were below detection limit by the GC/MS methods of analyses employed. Those materials detected were further verified by GC/MS/MS analyses. Two of the 290 results were above the detection limit of 1 ppb; naphthalene was found in one paving sample (1.8 ppb) and phenanthrene was measured in another paving sample at 1 ppb.

The National Cooperative Highway Research Program sponsored a research team at Oregon State University to develop a methodology to screen common highway construction and repair materials for potential impact on the quality of surface and ground waters. Results of laboratory testing and a first-level screening tool are presented in a series of U.S. Government publications. The study reported that “The materials conventionally used in pavements have been found to pose no harm to the environment.” The study further found that construction and repair materials containing crumb rubber, shingles, foundry sand and municipal solid waste incinerator bottom ash
“…exhibit[ed] significant toxicity …” to algae and daphnia. The study further found that “Toxicity is eliminated or greatly reduced in their amended forms (e.g. after incorporation into paving or fill) and even more so after sorption.”

The National Sanitation Foundation conducts testing of various materials for suitability for use in potable water system components, among its many functions. A listing of asphalt containing components certified for such use is maintained in a current state on the NSF website.63

Eurobitume carried out a study of the leaching behaviour of a paving grade bitumen and oxidised bitumen, together with a review of the available literature.64 The study evaluated release of heavy metals (As, Sb, Cd, Cr, Hg, Ni, Se, Al, Fe, Co, V, Mn), PAH, and BTEX (benzene, toluene, ethyl benzene and xylene). The results indicated that, with the exception of three PAHs (naphthalene, fluorene and phenanthrene), all analyses were below the detection limit. The PAH release was marginally above the detection limit, but was far below any regulatory limit for drinking water.

In 2004, researchers with the U.S. Geological Survey (USGS) published results of a study investigating the potential source(s) of PAHs and trace elements found in creek bed sediment near a seal-coated parking lot in Austin, Texas. Potential sources investigated included coal-tar-sealed, asphalt-sealed, unsealed asphalt and unsealed concrete pavements. Distilled deionized water was sprayed on sections of pavement under study in an attempt to simulate rainfall and the washoff was collected for analyses. PAH was reported to be highest for effluent from coal-tar-sealed plots of pavement followed by asphalt-sealed and unsealed plots. Based in part on these and similar reports from other locations, some U.S. cities, including Washington, D.C., have taken action to restrict the use of coal-tar sealants. Research on this subject is continuing.65
Appendix 1 – Glossary

This glossary represents a consolidated collection of terms used in the bitumen industry. Not all of the terms listed below are used in this document, but are common expressions used in the bitumen supply chain.

% m
Percent by mass. The mass of material reflects the quantity of matter within a sample.

% w
Percent by weight. Weight is defined as the mass multiplied by the force of gravity (Earth gravity is approximately 9.8 m/s⁻¹).

ACID MODIFIED ASPHALT/BITUMEN
Bitumen modified by the addition of inorganic acids, typically phosphoric, or polyphosphoric acid.

AIR BLOWING
The process by which compressed air is blown into a BITUMEN feedstock typically at 230-260°C (446–500°F), sometimes in the presence of catalysts (typically ferric chloride, phosphoric acid, or phosphorus pentoxide). This process results in complex reactions which raise the softening point and viscosity of the bitumen. See OXIDISED BITUMENS.

AIR-BLOWN ASPHALTS
See OXIDISED BITUMENS

AIR-BLOWN BITUMENS
BITUMEN products produced by AIR BLOWING. See OXIDISED BITUMENS.

AIR-REFINED BITUMENS
Penetration bitumens produced by partial blowing. Archaic term, no longer in use.

AIR-RECTIFIED BITUMEN (synonym SEMI-BLOWN BITUMEN)
A bitumen that has been subjected to mild oxidation with the goal of producing a bitumen meeting paving grade bitumen specifications. Air rectified bitumens are used in paving applications as well as roofing applications, such as shingle saturants and Type 1 Built Up Roofing Asphalt (BURA), and also for some industrial applications

ASPHALT
A mixture of BITUMEN and mineral materials used as a paving material that is typically produced at temperatures in the range of 140-160°C (280-320°F). In North America the term ASPHALT is synonymous with BITUMEN as used in Europe and also the term HOT MIX ASPHALT.

ASPHALT Binder
Term used in the U.S. and some other countries for BITUMEN.

ASPHALT CEMENT
Term used in the U.S. and some other countries for BITUMEN.

ASPHALT COLD MIXES
ASPHALT mixtures made using CUTBACK BITUMENS or BITUMEN EMULSIONS, which can be placed at ambient temperatures.

ASPHALTENES
Highly polar aromatic materials. Asphaltenes have high viscosity or stiffness at ambient temperatures and are responsible for the overall stiffness of BITUMENS. They can be precipitated with n-heptane and are sometimes referred to as n-heptane insolubles.

ASPHALT MASTIC
Asphalt mastic (AM) is a voidless asphalt mixture with bitumen as a binder containing filler and/or limestone fine aggregates and/or natural asphalt and/or sand (see EN 12970).
ASPHALT MIXES (MIXTURES)
Mixtures of graded mineral aggregates (sized stone fractions, sands and fillers) with a controlled amount of PENETRATION GRADED BITUMEN.

ATMOSPHERIC DISTILLATION
Distillation at atmospheric pressure

ATMOSPHERIC RESIDUE
Residue of ATMOSPHERIC DISTILLATION

BASE OILS
Petroleum-derived products consisting of complex mixtures of straight and branch-chained paraffinic, naphthenic (cycloparaffin) and aromatic hydrocarbons, with carbon numbers of 15 or more and boiling-points in the range of 300–600°C (570–1110°F). Depending on climatic conditions BASE OILS can be used to reduce the low stiffness of BITUMENS to resist low temperature cracking of pavements.

BENDING BEAM RHEOMETER
A machine used to determine the low temperature stiffness properties of BITUMENS that have been laboratory aged to simulate extended aging of the BITUMEN in ASPHALT pavements. Results are part of the PERFORMANCE GRADED BITUMEN specification

BINDER
According to EN12597: Material serving to adhere to aggregate and ensure cohesion of the mixture. A more general term used to identify BITUMEN plus potential modifiers used to produce ASPHALT mixes. The term BINDER reflects that some ASPHALT mixes may utilize MODIFIED BITUMENS.

BITUMEN BLOCKS
Small size blocks (typically 20kg) of BONDING BITUMEN for being melted in kettles

BITUMEN, PETROLEUM DERIVED
A dark brown to black cement-like residuum obtained from the distillation of suitable CRUDE oils. The distillation processes may involve one or more of the following: atmospheric distillation, vacuum distillation, steam distillation. Further processing of distillation residuum may be needed to yield a material whose physical properties are suitable for commercial applications. These additional processes can involve air oxidation, solvent stripping or blending of residua of different stiffness characteristics.

BITUMEN EMULSION
A mixture of two normally immiscible components (BITUMEN and water) and an emulsifying agent (usually a surfactant). Bitumen emulsions are utilized in paving, roofing and waterproofing operations. These materials are called EMULSIFIED ASPHALTS in North America.

BITUMEN FUME
The gases and vapors emitted from heated BITUMEN, and the aerosols and mists resulting from the condensation of vapors after volatilisation from heated BITUMEN.

BITUMEN GRADING TERMINOLOGY
There are currently three main grading systems employed world-wide for identifying and specifying bitumens used in road construction. These systems are PENETRATION, VISCOSITY and PERFORMANCE GRADED. Although each system has test methods that are unique to that system, similar bitumens are used across all grading systems. The particular system used within a given country or region is generally a result of historical practices or governmental stipulations.

BITUMEN ENAMEL (BITUMEN PAINT)
An external coating for protecting steel pipes. The term can also be used for bitumen paints (formulated CUTBACK BITUMENS or BITUMEN EMULSIONS)

BITUMEN MACADAM
A type of ASPHALT mix with a high stone content and containing 3–5% by weight of bitumen

BITUMEN PAINT
A CUTBACK BITUMEN made to treat bare metal or concrete or wood surfaces giving a bond between the surface and an ENAMEL or a bituminous membrane or bonding bitumen
BITUMEN PAINT
A specialized CUTBACK BITUMEN product that contains relatively small amounts of other materials that are not native to BITUMEN or to the diluents typically used in cutback products, such as lampblack, aluminum flakes, and mineral pigments. They are used as a protective coating in waterproofing operations and other similar applications.

BITUMEN PRIMER
A CUTBACK BITUMEN made to treat bare metal surfaces giving a bond between the metal and an ENAMEL.

BITUMEN ROOFING FELT
A sheet material, impregnated with BITUMEN, generally supplied in rolls and used in roof construction.

BITUMINOUS
Of or related to BITUMEN. In this document the terms BITUMEN and BITUMINOUS refer exclusively to petroleum derived BITUMEN as defined above.

BLENDED BITUMENS
Blends of two or more BITUMENS with different physical characteristics or blends of Bitumen(s) and high boiling point petroleum fractions (e.g. Heavy Vacuum Gas Oil) in order to achieve desired physical properties.

BLOWING STILL
(Also known as OXIDISER or Bitumen Blowing Unit.) Equipment used to air blow BITUMEN.

BONDING BITUMEN
OXIDISED BITUMEN or POLYMER MODIFIED BITUMEN used for HOT APPLIED ROOFING.

BRIQUETTE
See BRIQUETTING. Archaic term, no longer in use.

BRIQUETTING
The process by which fine materials (e.g., coal dusts, metal tailings) are mixed with a bitumen (or other) binder to form conveniently handled blocks or pellets. Archaic term, no longer in use.

BUILT UP ROOFING (BUR)
NORTH AMERICA:
A continuous roofing membrane consisting of plies of saturated organic (e.g., cellulose) felts or coated inorganic (e.g., glass fiber) felts, assembled in place with alternate layers of BITUMEN or COAL TAR PITCH, and surfaced with mineral aggregate, a granule surfaced sheet, or a roof coating.

EUROPE:
A continuous roofing membrane consisting of plies of coated inorganic (e.g., glass fiber) felts, assembled in place with alternate layers of BITUMEN, and surfaced with mineral aggregate, a granule surfaced sheet, or a roof coating.

BUILT UP ROOFING ASPHALT (BURA)
OXIDISED BITUMEN used in the construction of low slope built up roofing (BUR) systems; specification defined by ASTM D312. This material is called Built-Up Roofing ASPHALT (BURA) in North America.

CAS REGISTRY
A large database of chemical substance information in the world containing more than 29 million organic and inorganic substances and 57 million sequences. http://www.cas.org/

CAS REGISTRY NUMBER
A CAS Registry Number is assigned to a substance when it enters the CAS REGISTRY database.

CATALYTIC AIR-BLOWN BITUMENS
OXIDISED BITUMENS produced using catalysts in AIR BLOWING.

COAL TAR
A dark brown to black, highly aromatic material manufactured during the high-temperature carbonization of bituminous coals which differs from bitumen substantially in composition and physical characteristics. It has previously been used in the roofing and paving industries as an alternative to BITUMEN.

COAL TAR PITCH
A black or dark brown cementitious solid that is obtained as a residue in the partial evaporation or fractional distillation of COAL TAR. Coal Tar Pitch has been used in the past in roofing as an alternative to BITUMEN.
COATING BITUMEN
An AIR BLOWN or OXIDISED or polymer modified bitumen used to manufacture roofing membranes or shingles

COLD ADHESIVE
Bituminous CUTBACK used as a glue for application at ambient temperature of polymer modified bitumen membranes

COLD-APPLIED ROOFING BITUMEN
Bitumen roofing products that are applied at ambient temperatures at the work place without any heating (e.g. peel and stick bitumen membrane or membranes applied with the use of a cold adhesive)

COLLOID MILLS
High-speed shearing devices in which hot bitumen can be dispersed using a surfactant in an aqueous solution to produce a BITUMEN EMULSION

COLOURED MINERAL GRANULES
Natural or factory colored minerals used as light surface protection for bitumen membranes or bitumen shingles.

CRACKING-RESIDUE BITUMENS [THERMAL BITUMENS]
Archaic term, no longer in use

CRUDE OIL
See CRUDE PETROLEUM.

CRUDE PETROLEUM
A naturally-occurring mixture, consisting predominantly of hydrocarbons but also containing sulphur, nitrogen or oxygen derivatives of hydrocarbons, which can be removed from the earth in a liquid state

CUTBACK BITUMENS (PETROLEUM)
Bitumen whose viscosity has been reduced by the addition of a CUTBACK SOLVENT derived from petroleum.

CUTBACK SOLVENT (PETROLEUM)
Relatively volatile petroleum solvent used in the manufacture of CUTBACK BITUMEN. Typically white spirit (Stoddard Solvent) and kerosene are the petroleum derived solvents employed.

CYCLICS (NAPHTHENE AROMATICS)
Compounds with aromatic and naphthenic nuclei with side chain constituents. They are viscous liquids and represent the major proportion of the dispersion medium for the ASPHALTENES and adsorbed resins in bitumen. They constitute 30–60% by mass of the total bitumen,

DRUM-MIXER
An ASPHALT mixing device in which mixtures of MINERAL AGGREGATE and bitumen are heated and combined continuously in a rotating drum.

DYNAMIC SHEAR RHEOMETER
A testing device used to determine the stiffness of bitumens over a range of temperatures and test frequencies. Typically a standard amount of bitumen (25 mm in diameter by 1 mm in thickness) tested between two flat plates (25 mm in diameter). An oscillatory stress or strain of known value is applied to the bitumen sample and the resultant strain or stress is measured. From these data the stiffness of the bitumen is calculated. The stiffness results are part of the specification within the PERFORMANCE GRADED system of specifications.

DURABILITY TESTING
See WEATHERING TEST

EINECS
European INventory of Existing Commercial chemical Substances; analogous to the CAS system by which chemical substances were registered under the EU Existing Substances Regulation.

ELASTOMER
A polymeric substance (natural or synthetic) which when stretched to a length that is less than its point of rupture and released will recovery substantially to its originally length. Examples are vulcanized natural rubber, styrene butadiene latex rubber, styrene butadiene styrene block copolymer.
EMULSIFIED ASPHALTS
See BITUMEN EMULSIONS.

EQUIVISCOUS TEMPERATURE (EVT)
The temperature at which BITUMEN has a viscosity that is optimum for application in BUILT UP ROOFING (BUR) systems. For mop application the optimum apparent viscosity is 125 centipoise (cP), for mechanical application it is 75cP.

FILLER (Paving)
Fine mineral matter employed to give body to a bituminous binder or to fill the voids of a sand.

FILLER (Roofing)
Fine mineral matter, typically limestone, or slate dust mixed with BITUMEN prior to being applied as a coating in the manufacture of ROOFING SHINGLES and other roofing products.

FLASHPOINT
The temperature at which a combustible vapor forms above the surface of BITUMEN in a specific test method. Methods used for ROOFING BITUMEN products are EN ISO 2592 or ASTM D92 for Open Cup Flashpoint and EN ISO 2719 or ASTM D93 for Closed Cup Flashpoint.

FLEXIBLE PAVEMENTS
Road surfacings made from layers of ASPHALT mixes

FLUXED BITUMEN (PETROLEUM)
A bitumen whose viscosity has been reduced by the addition of a flux oil derived from petroleum. Note: Typically gas oils of various distillation ranges are employed as the flux oil. FLUXED BITUMEN differs from CUTBACK BITUMENS which also are reduced viscosity BITUMENS in that the flux oils have negligible volatility at ambient temperatures compared to the petroleum solvents used to produce CUTBACK BITUMENS

FLUX
This term has different meanings in different regions. e.g;

North America: also referred to as ROOFING FLUX. A term of art referring to a raw material from which OXIDISED BITUMEN is made. Typically soft bitumens [less than 50 Pa.s @ 60°C (140°F)] are used, although bitumens of higher viscosity can be included within the definition of FLUX.

Europe: FLUX refers to FLUX or FLUX OIL; Relatively involatile fluid (oil) used in the manufacture of fluxed bitumen.

FLUX OILS (PETROLEUM)
This term has different meanings in different regions. e.g.: 

North America: High flashpoint hydrocarbon oils (generally paraffinic) added to a ROOFING FLUX prior to oxidizing. The purpose of a FLUX OIL is to enable manufacture of OXIDISED BITUMEN with higher penetration values at a given softening point than would be possible without incorporation of the FLUX OIL.

Europe: FLUX refers to FLUX or FLUX OIL; Relatively involatile fluid (oil) used in the manufacture of fluxed bitumen, it also refers to the diluent used in the manufacture of OXIDISED BITUMEN.

FOREMAN
Supervises a crew or a particular operation in the placement and compaction process of asphalt.

FUME SUPPRESSING BUR BITUMENS
Proprietary BUR BITUMEN products which contain small amounts of polymer (added during manufacture or at the jobsite) that forms a layer on the surface of the heated BITUMEN, lowering the rate of fume generation. Also known as Low Fuming BITUMENS.

GAS OIL
A liquid petroleum distillate with a viscosity and boiling-range between those of KEROSENE and lubricating oil.

GILSONITE
A natural, resinous hydrocarbon found in the Uintah Basin in north eastern Utah, USA.

GLASS MAT OR FELT
A nonwoven mat made with short glass fibers adhered together with a resin and suitable for coating and impregnation with BITUMEN for roofing products.
HARD BITUMEN
A bitumen possessing low penetration value and high softening-point. These are used in the manufacture of high modulus ASPHALT MIXTURES.

HOT-APPLIED ROOFING
Application of roofing membranes with hot BONDING BITUMEN as a glue by mopping, pouring, or with mechanical spreaders (pour & roll technique). This is also called HOT BONDING ROOFING.

HOT BONDING ROOFING
See HOT APPLIED ROOFING.

HOT MIX ASPHALT
A mixture of bitumen and mineral materials used as a paving material that is typically produced at temperatures in the range of 140-160°C (280-320°F). In Europe, the term is synonymous with ASPHALT.

HOT WELDING ROOFING
See TORCHING.

KEROSENE (KEROSINE)
A petroleum distillate consisting of hydrocarbons with carbon numbers predominantly in the range of C9 through C16 and boiling in the range of 150–290°C (300–550°F).

LABORERS
Sometimes perform raker tasks and may be on site to perform miscellaneous tasks.

LAKE ASPHALT
Most common form of NATURAL ASPHALT, occurring in Trinidad.

LOSS ON HEATING
A common industrial BITUMEN test which measures the weight loss after exposing a small BITUMEN sample to 163°C (325°F) for 5 hours. See ASTM D6.

LOW-SLOPE ROOFING
Roofing products designed for a roof slope of less than or equal to 14 degrees.

MALtenes
Relatively low molecular weight oily fraction of bitumen. The maltenes are believed to dissolve, or disperse the ASPHALTENES in the colloidal structure of bitumen. They are the n-heptane soluble fraction of bitumen.

Mastic asPhalt
Mastic asphalt (MA) is a voidless asphalt mixture with bitumen as a binder in which the volume of the filler and binder exceeds the volume of remaining voids (see EN13108-6).

MEMBRANE
A factory made flexible layer of bitumen with internal or external incorporation of one or more carriers, supplied in roll form ready for use.

MINERAL AGGREGATE
A combination of stone fractions and FILLER.

MODIFIED BITUMENS
Bituminous binder whose rheological properties have been modified during manufacture by the use of one or more chemical agents.

MOPPER
A worker who spreads hot bitumen on a roof with a mop.

NATURAL ASPHALT
Naturally-occurring mixture of bitumens and mineral matter formed by oil seepages in the earth's crust. Natural asphalts include Trinidad Lake, Rock, Gilsonite, Selenice and others.

OXIDISED BITUMEN. (OXIDIZED BITUMEN)
Bitumen whose rheological properties have been substantially modified by reaction with air at elevated temperatures. This material is also sometimes referred to as “blown bitumen” and, in the USA, AIR-BLOWN ASPHALT.
OXIDISED BITUMEN MEMBRANE
A ROOFING BITUMEN product typically made by coating a glass fiber or polyester mat with a mixture of OXIDISED BITUMEN and mineral filler, and then packaging the finished product in rolls. In North America these products may be made with a mineral granule surface and are called “ROLL ROOFING”.

OXIDISER
See BLOWING STILL.

PAH, PAC
Polycyclic Aromatic Hydrocarbons is the collective name for a large group of several hundred chemicals that have a characteristic structure of two or more fused aromatic rings. They are a class of organic compounds and also a subgroup of the larger family of chemicals - Polycyclic Aromatic Compounds (PAC).

PAVER OPERATORS (PAVERS)
Person stationed on top of the paving machine (placement machine) to drive it as it receives asphalt from delivery trucks and distributes it on the road prior to compaction by rolling.

PAVING BITUMEN/ASPHALT
A bitumen used to coat mineral aggregate, mainly used in the construction and maintenance of paved surfaces and hydraulic works.

PAVING MACHINE
A machine designed for placement a uniform asphalt mat onto a road surface prior to roller compaction.

PENETRATION GRADED BITUMENS
Bitumens classified by the depth to which a standard needle will penetrate the bitumen sample under specified test conditions. (see ASTM D5 and/or EN1426 for an explanation of the penetration test).

PENETRATION INDEX
Indication of the thermal susceptibility of a bituminous binder. The penetration index is calculated from the values of PENETRATION and the SOFTENING POINT. It is based on the following hypothesis of Pfeiffer and Van Doormael:
a) At the temperature of the softening point, the penetration of a bitumen is 800 dmm.
b) When the logarithm (base 10) of PENETRATION is plotted against temperature, a straight line is obtained, the slope A of which is defined by:

\[
A = \left( \frac{20 - I_s}{10 + I_s} \right) \times \frac{1}{50}
\]

A PENETRATION INDEX of zero is attributed to a bitumen with a PENETRATION at 25°C (77°F) of 200 dmm and a SOFTENING POINT of 40 °C (104°F).

PENETRATION TEST
Specification test to measure the hardness of bitumen under specified conditions. In which the indentation of a bitumen in tenths of a millimeter (dmm) at 25°C (77°F) is measured using a standard needle with a loading of 100 g and 5s duration. Details of the test can be found in ASTM D5 and/or EN 1426 as well as other sources.

PERFORMANCE GRADED BITUMENS
Bitumens classified based on the research results of the Strategic Highway Research Program (SHRP). PERFORMANCE GRADED (PG) specifications are based on the stiffness of the bitumen at the high and low temperature environment in which the bitumen will be expected to perform within pavement. Currently Performance Graded Bitumens are most widely utilized in the United States and Canada.

PETROLEUM PITCH
The residue from the distillation of thermal cracked or steam-cracked residuum and/or catalytic cracked clarified oil with a SOFTENING POINT from 40 °C – 180 °C (104 °F – 356 °F). Composed primarily of a complex combination of three or more membered condensed ring aromatic hydrocarbons.

PLASTOMER
A polymer type which exhibits stiffness and strength but does not recover substantially when deformed. Examples of this type of polymer used in bitumens are ethylene vinyl acetate, ethylene methacrylate, polyethylene, and atactic polypropylene.
PLY
A layer of felt or sheet in a roof membrane; a four-ply membrane has at least four plies of felt or sheet at any vertical cross section cut through the membrane.

POLYMER MODIFIED BITUMEN/ASPHALT (PMB/A)
Modified Bitumen/Asphalt in which the modifier used is one or more organic polymers.

POLYMER MODIFIED BITUMEN MEMBRANE
A factory made flexible layer of STRAIGHT RUN and/or OXIDISED bitumen modified with elastomeric or plastomeric polymers with internal or external incorporation of one or more carriers, supplied in roll form ready for use.

POLYPHOSPHORIC ACID (PPA)
CAS No.: 8017-16-1, Molecular Formula: $\text{H}_6\text{P}_4\text{O}_{13}$. POLYPHOSPHORIC ACID includes long-chain polymerized units of PO$_4$ units. A key feature in POLYPHOSPHORIC ACID is the absence of free water.

PROPANE-PRECIPITATED ASPHALT (PROPANE BITUMEN)
See SOLVENT PRECIPITATION.

PUG-MILL
Mixer used to combine stone materials and bitumen in an asphalt-mixing plant. The mixing is effected by high-speed stirring with paddle blades at elevated temperatures.

RAFFINATE
The part of a liquid, especially an oil, remaining after its more soluble components have been extracted by a solvent.

RAKERMAN
Person who shovels and rakes excess HMA, fill in voids and prepare joints for compaction by rolling to ensure a road surface free from defects. Sometimes referred to as LABORER.

REFINERY
A facility composed of a group of separation and chemical engineering unit processes used for refining crude oil into different oil products.

RESINS (POLAR AROMATICS)
Very adhesive fractions of relatively high molecular weight present in the maltenes. They are dispersing agents (referred to as peptisers) for the ASPHALTENES. This fraction is separated using solvent precipitation and adsorption chromatography.

ROAD OILS
Term sometimes used for very soft VACUUM RESIDUE or harder BITUMENS that have FLUX OIL added, or CUTBACKS that have been produced using petroleum with a boiling point greater than 225°C (435°F) added to reduce the viscosity. ROAD OILS are generally used to produce ASPHALT paving mixes for use on very low volume roads in moderate to cold climates.

ROCK ASPHALT
Naturally-occurring form of ASPHALT, usually a combination of bitumen and limestone. Found in south-eastern France, Sicily and elsewhere

ROLL ROOFING
See OXIDISED BITUMEN MEMBRANE or POLYMER MODIFIED MEMBRANE.

ROLLER OPERATORS (ROLLERS)
Person driving machinery designed to compact the ASPHALT by rolling to finished specifications.

ROLLING THIN FILM OVEN TEST (RTFOT)
A common paving BITUMEN test which subjects a thin film of BITUMEN on the inside of a rolling glass jar to 163°C (325°F) for 85 minutes. See ASTM D2872, or EN 12607-1

ROOFER’S FLUX (also called ROOFING FLUX)
A low viscosity, high flashpoint, generally paraffinic residue of vacuum distillation of an appropriate petroleum crude oil used as a feedstock in the manufacture of OXIDISED BITUMEN used in roofing applications.
ROOFING BITUMEN/ASPHALT
Bitumen used for manufacture of roofing systems or roofing products, such as; bitumen shingles, BURA, POLYMER MODIFIED membranes, saturated felt underlayment, and roofing adhesives

ROOFING CEMENT
A material made by adding filler and fibres to either a BITUMEN EMULSION or CUTBACK BITUMEN to make an adhesive used for maintenance and in applying flashings on a new roof. Depending on the performance characteristics sought for particular cements, the BITUMEN used in the formulation may be OXIDISED or STRAIGHT-RUN.

ROOFING FELT
A sheet material, impregnated with BITUMEN, generally supplied in rolls and used in roof construction. See BITUMEN ROOFING FELT.

ROOFING KETTLE
A vessel used to heat binders such as OXIDISED BITUMEN for use in the construction of BUILT UP ROOFING and some POLYMER MODIFIED BITUMEN roof systems.

ROOFING SHINGLES
A STEEP-SLOPE ROOFING product. BITUMEN roofing shingles are typically made by coating a glass mat with filled COATING BITUMEN and then surfacing with colored mineral granules.

ROTARY DRUM DRYER
A device in an asphalt-mixing plant used to dry and heat stone materials

SATURANT BITUMEN
BITUMEN that is used to saturate organic felt to make roofing felt or to make organic based shingles. It can be STRAIGHT-RUN or OXIDISED BITUMEN.

SATURATES
Predominantly straight and branched-chain aliphatic hydrocarbons present in bitumens, together with alkyl naphthenes and some alkyl aromatics. This fraction forms 5–20% of the mass of bitumens

SCREED
Leveling device at the rear of a Paving machine.

SCREEDMAN
Person stationed at the rear of the paver, to control the distribution and grade of the ASPHALT mat as the paving machine moves forward

SELENICE
A NATURAL ASPHALT from Albania

SELF ADHESIVE BITUMEN MEMBRANE
Roofing or waterproofing polymer modified bitumen membrane applied at ambient temperature with the peel and stick method

SEMI-BLOWN BITUMEN
See AIR-RECTIFIED BITUMEN

SKIP-HOIST
A device for transfer of ASPHALT MIXES from a PUG-MILL to storage

SOFT-APPLIED ROOFING
BITUMEN roofing products that are applied by heating the BITUMEN membrane sufficiently with a torch or hot air welder to ensure good adhesion to the substrate.

SOFTENING-POINT
A specification test measuring the temperature, measured in °C, at which material under standardized test conditions attains a specific consistency. (See ASTM D36 and/or EN1427)

SOLVENT EXTRACTS
Aromatic by-products (extracts) obtained from the refining of BASE OILS
SOLVENT PRECIPITATION
The process by which a hard product, PROPA NE-PRECIPITATED ASPHAL T, is separated from a vacuum residue by solvent precipitation (usually with propane). PROPA NE-PRECIPITATED ASPHAL T is truly a bitumen by the definitions applied in this monograph. In the USA, this process is called ‘solvent deasphalting’ and the product, SOLVENT-REFINED ASPHAL T.

SOLVENT-REFINED ASPHAL T
Term used in the USA for PROPA NE-PRECIPITATED ASPHAL T, also referred to PDA pitch or PDA asphalt

STEAM-REFINED BITUMENS
VACUUM RESIDUES that have been subjected to STEAM STRIPPING

STEAM STRIPPING
Injection of steam into a residue which aids VACUUM DISTILLATION

STONE MASTIC ASPHALT, STONE MATRIX ASPHALT (SMA)
Referred to as STONE MASTIC ASPHALT in Europe or STONE MATRIX ASPHALT in the United States. SMA is a gap-graded asphalt mixture with bitumen as a binder, composed of a coarse crushed aggregate skeleton bound with a mastic mortar (In Europe SMA is specified by EN 13108-5, in the USA it is specified regionally by State Highways Agencies). It is paved at temperatures typically employed for conventional ASPHAL T mixtures.

STEEP-SLOPE ROOFING
Roofing products designed for a roof slope of more than 14 degrees.

STRAIGHT-REDUCED BITUMENS
VACUUM RESIDUES used as bitumens. STEAM STRIPPING may have been used in their production. STRAIGHT REDUCED BITUMENS refer to a bitumen produced to a specific target grade without blending with other bitumen grades to achieve the desired result.

STRAIGHT-RUN BITUMENS
Similar to STRAIGHT-REDUCED BITUMENS and STEAM-REFINED BITUMENS

SULPHUR EXTENDED ASPHAL T
A hot mixed asphalt in which part of the bituminous binder is replaced by elemental sulphur, typically at levels between 20–40% of the original bitumen content.

SURFACE DRESSING
Process used to seal road surfaces; a thin film of bitumen, CUTBACK BITUMEN or BITUMEN EMULSIONS is spread, covered with a single or double layer of chippings, and then rolled.

SURFACE TREATMENT
May include SURFACE DRESSING and other techniques, such as spraying with minor amounts of BITUMEN EMULSION to bind surfaces together

TEAR OFF
To remove an existing roof system for replacement.

TERMINAL
A facility outside a refinery where bitumen is held for intermediate storage prior to delivery to (or collection by) customers.

THERMALLY CRACKED BITUMENS
Also known as Residues (petroleum), thermal cracked, vacuum: Bitumens produced by thermal cracking

Topping Plant
A ‘stand alone’ distillation plant. Topping plants are usually found in terminals and used to remove distillate materials added to bitumens for transportation purposes.

TORCHING
Application of a roofing membrane with a propane gas flame, used for melting the side of the roofing membrane, without addition of hot bonding bitumen. This is also called HOT WELDING ROOFING
TRINIDAD LAKE ASPHALT
A NATURAL ASPHALT obtained from the La Brea region of Trinidad

UNDERLAYMENT
Factory made flexible sheets of bitumen (OXIDISED or MODIFIED) which are used as underlay to coverings of sloping roofs (e.g. tiles, slates, shingles)

VACUUM DISTILLATION
Distillation of ATMOSPHERIC RESIDUE under vacuum.

VACUUM RESIDUE
Residue obtained by VACUUM DISTILLATION

VISBREAKING
A relatively mild thermal cracking operation mainly used to reduce the viscosity and pour point of vacuum residues for subsequent use in heavy fuel oils. The process converts a proportion of the residue feedstock to distillate product, e.g. Gas oil.

VISCOSITY
Resistance to flow of a substance when a shearing stress is imposed on the substance. For BITUMEN products, test methods include vacuum-capillary, cone and plate, orifice-type and rotational viscometers. Measurements of viscosity at varying temperatures are used by technologists in all industry segments that utilize BITUMEN materials

VISCOSITY-GRADED BITUMEN
BITUMEN which is graded and specified by the viscosity at a standard temperature, which is typically 60 °C (140°F). ASTM D2171 and EN 12596 are the most commonly used viscosity tests.

WARM MIX ASPHALT
Asphalt mixtures produced at lower temperatures as compared to those typically associated with rolled asphalt pavement. Warm-mix asphalts are produced and placed at temperatures typically 10 – 40 ºC (50 – 100 ºF) lower than conventional rolled asphalt.

WEATHERING TEST
Various accelerated durability tests have been developed for OXIDISED BITUMENS used in roofing applications. The most prevalent is the Xenon Arc Accelerated Weathering test, where thin OXIDISED BITUMEN films are applied to aluminum panels and then subjected to light, heat, and water sprays in several combinations of time and temperature. See ASTM D4798, ASTM D1669, and ASTM D1670.

WHITE SPIRIT
A distillate petroleum product free of rancid or objectionable odors, boiling-range 150-200 °C (300-390 °F); sometimes described as ‘Stoddard solvent’
### Appendix 2 - CAS and EINECS descriptions for commonly used bitumens

#### 1. Bitumen Entries in the European Inventory of Existing Commercial chemical Substances (EINECS). These entries were registered under the European Existing Substances Regulation [COUNCIL REGULATION (EEC) No 793/93]

<table>
<thead>
<tr>
<th>EINECS number</th>
<th>CAS Registry Number</th>
<th>Description</th>
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<tbody>
<tr>
<td>232 - 490 - 9</td>
<td>8052 - 42 - 4</td>
<td>Asphalt</td>
</tr>
<tr>
<td>265 - 057 - 8</td>
<td>64741 - 56 - 6</td>
<td>Residues (petroleum), vacuum</td>
</tr>
<tr>
<td>265 - 188 - 0</td>
<td>64742 - 85 - 4</td>
<td>Residues (petroleum), hydrodesulfurized vacuum</td>
</tr>
<tr>
<td>265 - 196 - 4</td>
<td>64742 - 93 - 4</td>
<td>Asphalt, oxidized</td>
</tr>
<tr>
<td>295 - 284 - 8</td>
<td>91995 - 23 - 2</td>
<td>Asphaltenes (petroleum)</td>
</tr>
<tr>
<td>295 - 518 - 9</td>
<td>92062 - 05 - 0</td>
<td>Residues (petroleum), thermal cracked vacuum</td>
</tr>
<tr>
<td>302 - 656 - 6</td>
<td>94114 - 22 - 4</td>
<td>Residues (petroleum), dewaxed heavy paraffinic, vacuum</td>
</tr>
<tr>
<td>309 - 712 - 9</td>
<td>100684 - 39 - 7</td>
<td>Residues (petroleum), distn. residue hydrogenation</td>
</tr>
<tr>
<td>309 - 713 - 4</td>
<td>100684 - 40 - 0</td>
<td>Residues (petroleum), vacuum distn. residue hydrogenation</td>
</tr>
</tbody>
</table>

A very complex combination of high molecular weight organic compounds containing a relatively high proportion of hydrocarbons having 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.
2. Bitumen (Asphalt) category members in US Environmental Protection Agency’s High Production Volume chemicals testing program. All substances are listed on US Inventory (Toxic Substances Control Act, 15 U.S.C. s/s 2601 et seq. 1976).

**Asphalt (CAS# 8052-42-4)**
A very complex combination of high molecular weight organic compounds containing a relatively high proportion of hydrocarbons having 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.

**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.

**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).

**Petroleum Resins (CAS# 64742-16-1)**
A complex combination of organic compounds, predominantly hydrocarbons, obtained as a fraction of the extract from 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 sulphur compounds. It consists of hydrocarbons having carbon numbers predominantly greater than C34 and boiling approximately above 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).

3. Carcinogen Classification of Bitumen by Various Agencies and Authorities

<table>
<thead>
<tr>
<th>Agency</th>
<th>Substance</th>
<th>Classification</th>
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</thead>
<tbody>
<tr>
<td>American Conference of Governmental Industrial Hygienists</td>
<td>Asphalt (bitumen) fumes</td>
<td>A4 - Not Classifiable as a Human Carcinogen</td>
</tr>
<tr>
<td>International Agency for Research on Cancer (1985)</td>
<td>Bitumens</td>
<td>Group 3 - Not Classifiable</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Group 2B - Possibly Carcinogenic to Humans</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Inadequate human evidence</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Inadequate animal evidence</td>
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<tr>
<td></td>
<td></td>
<td>Limited animal evidence</td>
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<td>Sufficient animal evidence</td>
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<td></td>
<td></td>
<td>Sufficient animal evidence</td>
</tr>
<tr>
<td>California Safe Drinking Water and Toxic Enforcement Act</td>
<td>Extracts of steam-refined and air refined bitumens</td>
<td>Listed as carcinogen</td>
</tr>
<tr>
<td>European Union Classification</td>
<td>Asphalt</td>
<td>Not classified</td>
</tr>
<tr>
<td>US National Institute for Occupational Safety and Health</td>
<td>Asphalt Fumes</td>
<td>NIOSH Carcinogen List</td>
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<tr>
<td>US National Toxicology Program</td>
<td>Asphalt Fumes</td>
<td>Evaluation deferred</td>
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### Appendix 3 - Summary of refinery sector exposure data

<table>
<thead>
<tr>
<th>Occupation</th>
<th>Source of exposure</th>
<th>Number</th>
<th>Type</th>
<th>Range</th>
<th>Geo. Mean</th>
<th>Ari. mean</th>
<th>Ref</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>General asphalt refinery workers</td>
<td>Vacuum distillation</td>
<td>4°</td>
<td>Total PAHs†</td>
<td>0.0047-0.016</td>
<td>0.0082</td>
<td>0.0095</td>
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<td>NIOSH Hazard Review</td>
</tr>
<tr>
<td>General asphalt refinery workers</td>
<td>Asphalt processing (6 refineries)</td>
<td>14°</td>
<td>Total PAHs†</td>
<td>0.0015-0.031</td>
<td>0.067</td>
<td>0.010</td>
<td>NIOSH 1983 65</td>
<td>NIOSH Hazard Review</td>
</tr>
<tr>
<td>General asphalt refinery workers</td>
<td>Deasphalting (1 refinery)</td>
<td>4°</td>
<td>Total PAHs†</td>
<td>0.0014-0.041</td>
<td>0.12</td>
<td>0.021</td>
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<td>NIOSH Hazard Review</td>
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<tr>
<td>Assistant operator</td>
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<td>3</td>
<td>Total PAHs†</td>
<td>0.0025-0.050</td>
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<td>0.025</td>
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<tr>
<td>Bitumen loaders</td>
<td>Outdoor bitumen refinery unit (bitumen at 170 to 210°C [338 to 410°F])</td>
<td>4</td>
<td>Benzene solubles</td>
<td>0.3-1.0</td>
<td>5</td>
<td>5</td>
<td>Claydon et al.1984 44</td>
<td>NIOSH Hazard Review</td>
</tr>
<tr>
<td>Bitumen loaders</td>
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<td>4</td>
<td>Total particulates</td>
<td>0.1-1.4</td>
<td>5</td>
<td>5</td>
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<td>NIOSH Hazard Review</td>
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<tr>
<td>Package fillers</td>
<td>Indoor area (bitumen at 220°C [428°F])</td>
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<td>Total particulates</td>
<td>0.20-0.32</td>
<td>0.25</td>
<td>0.23</td>
<td>Brandt et al.1985 55</td>
<td>NIOSH Hazard Review</td>
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<tr>
<td>Bitumen loaders</td>
<td>Outdoor bitumen refinery unit (bitumen at 170 to 210°C [338 to 410°F])</td>
<td>4</td>
<td>Total particulates</td>
<td>0.7-2.9</td>
<td>5</td>
<td>1.4</td>
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<tr>
<td>Operator</td>
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<td>11</td>
<td>Total particulates</td>
<td>&lt;0.03-0.8</td>
<td>0.17</td>
<td>0.88</td>
<td>Hicks 1995 55</td>
<td>NIOSH Hazard Review</td>
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<tr>
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<td>11</td>
<td>Benzene solubles</td>
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<td>0.42</td>
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<td>NIOSH Hazard Review</td>
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<tr>
<td>Assistant operator</td>
<td>Asphalt refinery/terminal (temperature of product at fume source ranged from 160 to 375°C [320 to 707°F])</td>
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<td>Total particulates</td>
<td>&lt;0.03-0.49</td>
<td>0.18</td>
<td>0.25</td>
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<td>9</td>
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<td>NIOSH Hazard Review</td>
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<td>4</td>
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<td>4</td>
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<td>General Refinery Workers</td>
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<td>Boogaard et al 1995 65</td>
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<td>Refinery Road tanker loading</td>
<td>Various Pen and oxidised grades (170-210°C [338-410°F])</td>
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<td>Total particulates</td>
<td>0.7-2.9</td>
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<td></td>
<td>Brandt et al 55</td>
<td></td>
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<td>General refinery Workers</td>
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<td>Total PACs</td>
<td>1.8-19 µg/m³</td>
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<td>Futagaki et al 1981 70</td>
<td>IBRC mon #35 (same ref as NIOSH 1983)</td>
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<td>Office worker</td>
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<td>TPM</td>
<td>0.04-0.29</td>
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<td>0.08</td>
<td>Gamble 70</td>
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<td>Lab Technician</td>
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<td>TPM</td>
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<td>0.23</td>
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<td>0.07-0.58</td>
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<td>0.24</td>
<td>0.23</td>
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<td>4</td>
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<td>0.08-0.77</td>
<td>0.26</td>
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<tr>
<td>Occupation</td>
<td>Source of exposure</td>
<td>Number</td>
<td>Type</td>
<td>Range (mg/m³)</td>
<td>Geo. Mean</td>
<td>Ari. Mean</td>
<td>Ref</td>
<td>Source</td>
</tr>
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<td>Misc.</td>
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<td>Refinery/Terminal</td>
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<td>0.02</td>
<td>Hicks ‡</td>
<td>Further information to be found in full citation</td>
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<td>11</td>
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<td>0.03-2.51</td>
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<td>Driver / Loader</td>
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<td>Plant operator</td>
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<td>TPM</td>
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<td>NA</td>
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<td>Unpublished UK production facility 1999</td>
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<td>Driver / Loader</td>
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<td>0.6 – 3.0 mg/m³ 15 min STEL</td>
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<td>4</td>
<td>TPM</td>
<td>0.09 - 0.27</td>
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<td>0.18</td>
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<td>Shell Global Solutions</td>
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<td>BSF</td>
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<td>BSF</td>
<td>0.03 - 1.6</td>
<td>0.24</td>
<td>0.43</td>
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<td>10</td>
<td>SV</td>
<td>0.09 - 1.4</td>
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<td>6</td>
<td>T6 EPA-PAHs</td>
<td>1.09 – 10.68 μg/m³</td>
<td>2.57 μg/m³ 8hr TWA</td>
<td>3.51 μg/m³ 8hr TWA</td>
<td>Expositions Individuelles aux Fumées de Bitumes lors du Chargement de Citernes en Raffinerie</td>
<td>Groupement Professionnel des Bitumes 2010</td>
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<td>Truck driver</td>
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<td>Naphthalene</td>
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<td>Ba(a)P</td>
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<td>SV</td>
<td>0.55 1.45 mg/m³</td>
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</tbody>
</table>

TPM: Total Particulate Matters in mg/m³
BSF: Benzene Soluble Fractions in mg/m³
SV: Semi-Volatiles (gaseous fractions) in mg/m³

Abbreviations: Ari. mean=arithmetic mean; Geo. mean=geometric mean.

* Area air samples. All remaining samples were personal-breathing-zone air samples.
† The sampling and analytical methods used for measuring PAH concentrations may vary between studies and results may not be directly comparable.
‡ Number of samples collected not available.
§ Information not provided.

NOTE: Sampling periods ranged from 6 to 8 hours. Results shown are time-weighted averages.

NOTE: Solvents such as cyclohexane and acetonitrile have been used in place of benzene to measure the soluble fraction of a particular matrix. Because the extraction ability of these solvents varies, results are not comparable.

NOTE: Detailed information methods used to determine exposure can be found in the citations. It should be noted that the use of different analytical methods for determination of, e.g. Total Particulate Matter, or Benzene Soluble fraction, may give results that are not directly comparable.
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