THE BITUMEN INDUSTRY

A GLOBAL PERSPECTIVE

Production, chemistry, use, specification and occupational exposure

Fourth Edition

A Joint Publication of

asphalt institute | eurobitume

IS-230

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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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CONTENTS

1. SCOPE

This document describes the manufacture of bitumen, including blending and modification, focusing on North America and Europe. The types, chemistry, physical properties, health, safety, environment, and sustainability of bitumen are discussed from the manufacturers' perspective. This document covers bitumen produced by refining petroleum (crude oil), including those crude oils sourced and processed from oil sand and oil shale deposits. Although other bitumen-like deposits exist, such as natural asphalt, lake asphalt, and rock asphalt, the term "bitumen" in this document refers only to products obtained from petroleum through various refining processes. While comprehensive, it is only a summary of large amounts of scientifically verified and fact-based information related to bitumen. For further information, the user is encouraged to review the documents referenced or contact the Asphalt Institute or Eurobitume [1] [2].

2. INTRODUCTION

Bitumen is manufactured from the distillation of crude oil during petroleum refining. It is produced to meet various specifications based on physical properties for specific end uses. Bitumen's main characteristics, which are adhesivity, waterproofing, thermoplasticity, durability, ease of modification, reusability and recyclability, make it ideal as a construction and engineering material.

According to a report published by the International Bitumen Emulsion Federation (IBEF), the estimated world consumption of bitumen in 2022 was approximately 120 million tonnes (Figure 1). The IBEF regularly collects data on the consumption of bitumen and bitumen emulsions in most countries. Data accuracy varies from source to source (https://www.ibef.net/en/emulsions-2/key-figures/).

There are more than 250 known bitumen applications, with most of it being used in paving and roofing applications:

According to Figure 2, the largest end-use sector of bitumen is paving, with approximately 85% of all bitumen being used as a binder in various types of bitumen pavements, such as roads, airport runways, and parking lots[3, 4]. Around 10% of bitumen is used for roofing, including membranes, shingles, hot-applied built-up roofing, and cold-applied roll-on roofing[5]. The remaining 5% of bitumen is used for small volume applications such as sound and electrical insulation, water pipe coating, bitumen paints, waterproofing (excluding roofing), and sealing materials. This sector is known as "other applications".

Estimated global bitumen use - 2022

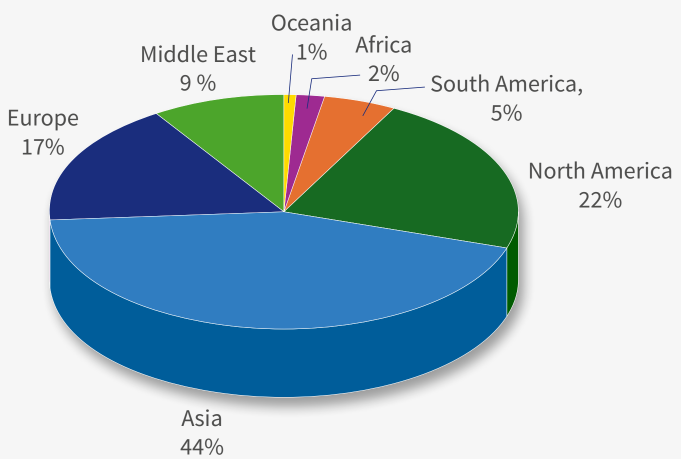

Figure 1. Estimated global bitumen use in 2022

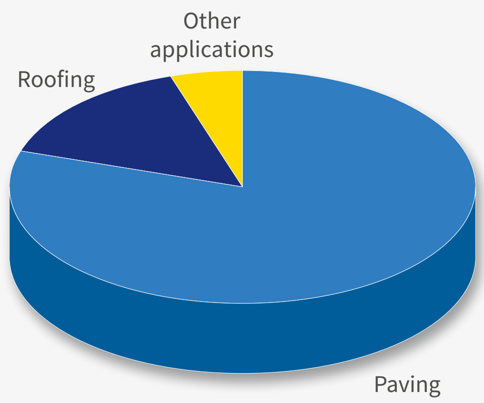

Figure 2. Proportion of use by application

Specifications for bitumen are partly based on regional climatic factors described in terms of engineering properties (consistency, stiffness, viscosity, material strength/cohesion, adhesion, and ageing/durability). Furthermore, since bitumen is commonly used in construction materials at high temperatures, its characteristics at these temperatures should also be considered.

The properties and characteristics of bitumen depend mainly on the crude oil and refining conditions used in its manufacturing. It is produced to grade specification by refining or by blending.

"Straight-run bitumen" is a term used for the residual product after vacuum distillation of crude oil. This residue can be further refined during the deasphalting process and blended with straight-run bitumen. To meet specific product requirements, bitumen can be processed by blowing air through it at high temperatures (air-rectification or oxidation), which changes its physical properties. Within the refinery, petroleum streams used for producing bitumen are classified by their Chemical Abstract Service (CAS#) Registry Number and/or European INventory of Existing Commercial chemical Substances (EINECS). Appendix 2 contains a summary of CAS#/EINECS numbers that have been or can be used for bitumen products.

Chapter 3 of this publication describes how bitumen is manufactured. Bitumen is generally not used on its own but as a component of, for example, asphalt mixtures and waterproofing membranes. Bitumen can also be modified using non-bituminous products, and examples are provided in Chapter 4. An overview of bitumen's physical properties and chemical composition is given in Chapter 5.

Bitumen is typically applied at elevated temperatures, which may give rise to emissions, which could lead to exposure in an occupational setting. Occupational exposure to bitumen emissions is strongly related to the temperature of application. Chapters 6 and 7 address health and safety considerations, including bitumen emissions and exposure measurements associated with working with hot bitumen.

Chapter 8 is a new chapter in this edition that describes the important sustainability aspects of bitumen.

2.1 Terminology

Petroleum bitumen is known by different names throughout the world. For example, the term "bitumen" is typically used in Europe and is synonymous with the term "asphalt" or "asphalt binder" used in North America. Outside North America, the term "asphalt" describes mixtures of bitumen with mineral aggregates. In this document, the term bitumen will be used to represent all bituminous products used in hot and warm applications.

Coal-derived products such as coal tar or coal-tar pitches are very different from bitumen. These are manufactured by the high-temperature pyrolysis (>800°C) of bituminous coals and differ from bitumen substantially in composition, physical characteristics, and potential health risks. These differences are well-defined in the literature [6] [7] [8].

Petroleum pitches [CAS# 68187-58-6], which are often highly aromatic residuums produced by thermal cracking, coking, or oxidation from selected petroleum fractions, are also significantly different chemically from bitumen.

Bitumen should not be confused with natural or lake asphalt such as Trinidad Lake Asphalt, Gilsonite, Rock Asphalt, or Selenice, which are sometimes used as additives in end-use applications. These products are unrefined and not produced by refining crude oils. 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[9]. A glossary of terms appears at the end of this document (Appendix 1).

2.2 Bitumen identification and specifications

Substance inventories vary by region due to differences in legislation. In Europe, nine CAS# numbers cover refinery streams that may be used in bitumen manufacturing. Not all nine are registered under the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) regulation (https://echa.europa.eu/regulations/reach). The majority of bitumen relates to three CAS# registry numbers:

- Asphalt [CAS# 8052-42-2],
- Residues Vacuum [CAS# 64741-56-6], and
- Asphalt, Oxidised [CAS# 64742-93-4][10].

In North America, all products in commerce are listed either on the United States Environmental Protection Agency (US EPA) Toxic Substances Control Act (TSCA), Canadian Domestic Substance List (DSL), or Non-Domestic Substances List (NDSL) and are identified in terms of three substances (“Asphalt”, “Asphalt Oxidised” and “Vacuum Residue”).

Systems to specify bitumen vary by region and application and are based on the physical properties of the bitumen. Specification systems are developed by national or regional standardisation bodies (e.g. AASHTO, ASTM, Standards Australia, CEN, and Standardization Administration of China). See Appendix 4 for standards and specifications.

3. BITUMEN MANUFACTURING

Bitumen is primarily obtained by vacuum distillation of carefully selected crude oil or blends of crude oils. It comprises the non-distillable fraction, often technically referred to as petroleum (vacuum) residue or residuum. In its simplest form, bitumen manufacturing separates the lighter, low boiling point fractions from crude oil, resulting in products with a very high boiling point and high molecular weight with very low volatility. The properties and quality of bitumen depend mainly on the crude oil(s) used and the refinery operating conditions. It is produced to grade specification either directly by refining or by blending. Bitumen can be further processed to alter its physical properties to meet certain specifications. Several manufacturing methods are available to produce bitumen depending on the crude source(s) and refining conditions available within a refinery [11] [12] [13]. Often, a combination of processes is selected.

3.1 Crude oil analysis and selection

Petroleum residuum from the distillation of crude oils is the starting material for bitumen production. Therefore, the properties of the bitumen depend upon the properties of the crude oil from which the bitumen is manufactured. Of the many commercially available crude oils or blends, only a limited number are considered suitable for producing bitumen of the required quality in commercial quantities. In general, heavy (Specific Gravity >0.9, American Petroleum Institute (API) Gravity <26°) crude oils are used to produce bitumen of the required quality. These types of crude oils tend to contain higher sulphur contents (>1%).

Typically, crude oils suitable for bitumen production have a bitumen content of 20 - 50% mass. 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 significantly. Further, the nature of petroleum refining processes means that bitumen from different sources of supply are expected to be qualitatively similar [14].

Bitumen could also be produced from hydrocarbons extracted from oil sands or oil shales.

3.2 Distillation

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

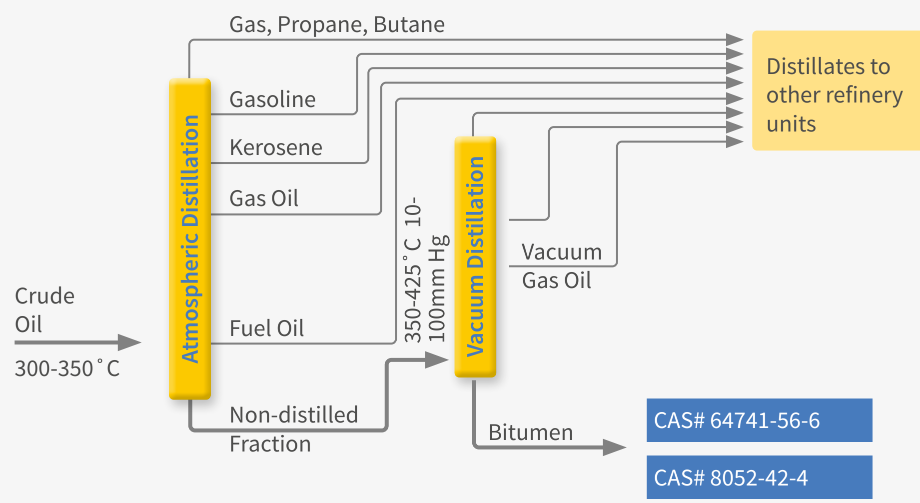

Figure 3. Schematic diagram of the distillation process

To remove the remaining lighter fractions and avoid thermal transformation of the molecules, atmospheric residuum is introduced into a vacuum distillation unit. At reduced pressure, more of the remaining lighter fractions can be separated as the boiling temperatures are lower; in this way, unwanted thermal cracking of the molecules is avoided.

The atmospheric equivalent temperature is calculated from the actual distillation temperature and pressure and indicates the temperature that would need to be reached in the atmospheric column to achieve comparable distillation conditions to those in the vacuum column[(15)]. The lighter fractions, for example, vacuum gas oils, are removed at atmospheric equivalent temperatures of 345-450°C, leaving a high boiling point and high molecular weight hydrocarbon residue. The atmospheric equivalent temperature to yield the vacuum residuum is typically around 538°C.

Depending upon the specification grade requirements, the vacuum residuum can be used directly, further processed, or as a component of blended bitumen.

The non-distillable materials produced by distillation of atmospheric residuum under vacuum are described by Asphalt [CAS# 8052-42-4] and Residues (petroleum), vacuum [CAS# 64741-56-6].

3.3 Air-rectification

A mild degree of air-blowing, known as air-rectification, is commonly used to make a minor adjustment to the physical properties, such as decreasing the penetration and/or increasing the stiffness and the softening point of the bitumen. The feedstock for air-rectification is vacuum residue and/or bitumen.

Air-rectified bitumen is predominantly used in paving applications but may also be used in roofing and industrial coating applications or as a base for manufacturing polymer-modified bitumen (PMB) and bitumen emulsions. Application temperatures for air-rectified bitumen are similar to those for paving grades. There is no differentiation between air-rectified and paving-grade bitumen conforming to the same specification. However, there are significant rheological differences between air-rectified and oxidised bitumen.

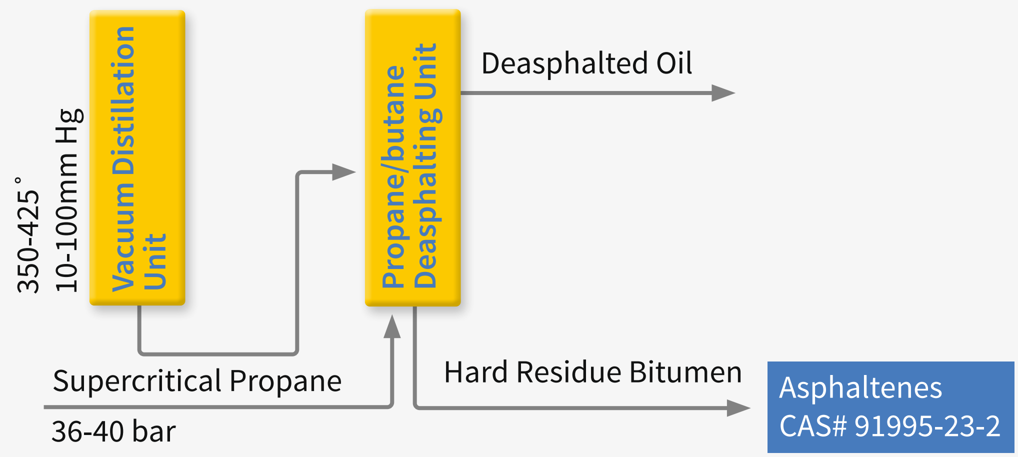

Figure 4. Schematic diagram of the propane deasphalting process

In Europe, air-rectified bitumen has a Penetration Index (PI) ≤ 2.0, while oxidised bitumen has a PI >2.0.

3.4 Solvent deasphalting

The properties of the vacuum residuum can be modified by using subsequent refining process steps. Solvent deasphalting or the Residual Oil Solvent Extraction (ROSE) process, uses propane, butane, isobutene, pentane, or supercritical extraction to separate asphaltene-type fractions from residuums used for producing lubricating oil base stocks [16]. The hard residue bitumen remaining after solvent deasphalting can be blended to produce bitumen conforming to the relevant specification.

The residual products produced by processing through a solvent deasphalting unit are described as Asphalt [CAS# 8052-42-4], Asphaltenes [CAS# 91995-23-2] and Petroleum Resins [CAS# 64742-16-1], depending upon the process used.

3.5 Vacuum distillation of thermally cracked residuum

Thermal cracking (also known as visbreaking) involves heating a suitable feedstock (atmospheric or vacuum residue) to 440-500°C at pressures between 6-11 bar. Process conditions vary depending on the feedstock and the desired properties of the thermally cracked material, avoiding coke formation.

When used for bitumen production, the thermally cracked residue is subjected to vacuum distillation to remove the distillate fractions. The product obtained after vacuum distillation is typically a hard material that can be used as a blending component for bitumen production.

3.6 Oxidation

Oxidised bitumen, also known as blown bitumen, is produced in a bitumen oxidation unit. This process involves passing 85-140 m^3/min of air through bitumen feedstock at elevated temperatures to significantly change the physical properties of the products.

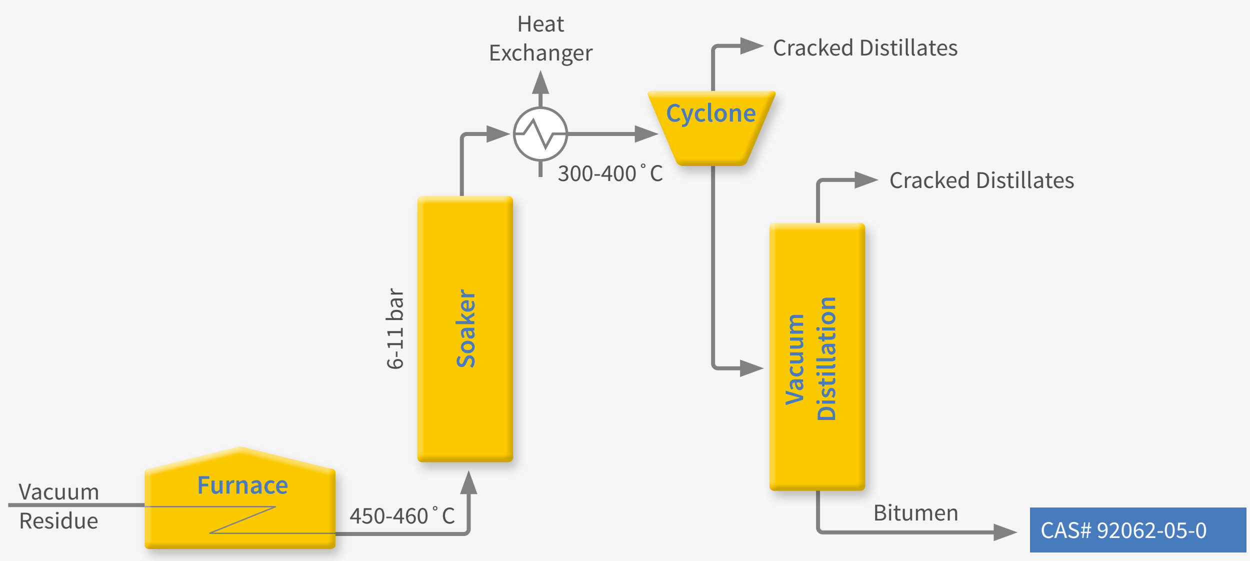

Figure 5. Schematic diagram of the thermal cracking process

The main purpose is to stiffen the bitumen, as measured by an increase in softening point, a decrease in penetration, and an increase in viscosity. The process achieves this through various chemical reactions, which result in an increase in the apparent molecular weight and polarity of the bitumen (17) (18) (19) (20) (21). A catalyst may be used to increase the rate of the reaction and improve the temperature susceptibility of the product relative to oxidation without a catalyst. Catalysts include materials such as ferric chloride, hydrochloric acid, phosphorous pentoxide, or phosphoric acid. Although referred to as catalysts, some materials used are consumed during the reaction and are, therefore, not true catalysts.

To achieve the expected properties of oxidised bitumen and, in particular, a very high softening point, it is necessary to use very soft feedstock (typically with a viscosity of less than 500 cSt at 100°C). In Europe, a flux (see glossary) is usually added to the feed to the oxidation unit to better control the viscosity (22).

The bitumen oxidation unit consists primarily of a reactor vessel, air blower, off-gas treatment facility, and temperature control equipment. The reactor is often a simple 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 temperature. Injection of steam/water into the reactor headspace may also reduce the oxygen content of the off-gases to manage the risk of fire or explosion.

The rate at which the oxidation reactions occur is affected by feedstock properties, e.g. viscosity, penetration, and reactivity. The reaction rate is also affected by the operating parameters of temperature, air flow rate, degree of agitation, pressure, air-to-feed ratio, and whether or not a catalyst is employed.

A schematic diagram of a bitumen oxidation unit is provided in Figure 6.

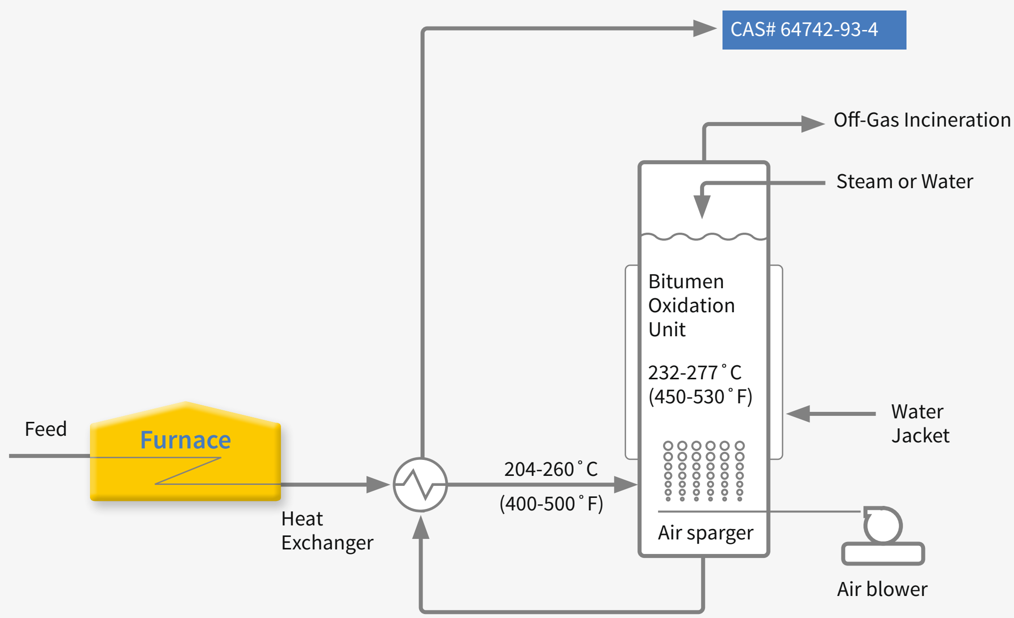

Figure 6. Schematic diagram of the bitumen oxidation process

3.7 Other refinery processes

Several other refinery processes are used to produce small amounts 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 refinery processes. The processes, including hydro desulphurisation and hydrogenation, are not commonly used and hence represent only a minor part of the overall bitumen production.

3.8 Bitumen blending

Bitumen is produced to meet specifications either directly in the refining process or by blending with bitumen having different physical properties. Higher viscosity products or bitumen may be blended with lower viscosity products or bitumen in suitable proportions to satisfy final specification requirements. Specifications are covered in section 2.2. Blending may take place at the refinery, 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.

Not all blends of bitumen streams during manufacture meet the definition of bitumen and are more appropriately considered mixtures. Guidance on the distinctions between bitumen substances and mixtures has been developed by Eurobitume for specific application to the European REACH regulation (10). Appropriate definition as bitumen or a mixture may have regulatory implications, including hazard classification and communication. Any hazard or risk transferred to a bitumen mixture from a component substance, for example, refinery streams rich in Polycyclic Aromatic Hydrocarbons (PAHs), should be identified, e.g. if above a regulatory threshold.

4. BITUMEN AND BITUMINOUS PRODUCTS

The primary use of bitumen worldwide is in the production of asphalt mixtures, where it is mixed with aggregates, fillers, and potentially other additives to produce durable, sustainable pavements, membranes, pipe coatings and sealing materials. Several other lower-volume applications also exist, including agricultural use and electrical and acoustic insulation. In most of these applications, bitumen typically comprises approximately 5-25% of the product.

The properties of bitumen can be modified by adding other components to improve performance. The history of bitumen modification closely follows that of bitumen itself. Modification techniques primarily depend on the final application's desired performance and product specifications. There are three general classifications of modified bitumen products: polymer modification, chemical modification and the addition of special fillers or extending agents.

Recycled materials used in bituminous applications include Reclaimed Asphalt Pavement (RAP) and other reclaimed/re-used bituminous materials such as Reclaimed Asphalt Shingles (RAS). Bitumen modified by other extender agents is also used in recycling applications. Virgin bitumen combined with RAP and/or RAS can produce new pavements. Often RAP and/or RAS containing mixtures are used in lower layers where ageing is less likely to occur. When used in lower layers, these aged bitumen materials can be used with reduced chances of pavement failure.

Research utilising rejuvenators derived from bio-based sources or petroleum streams is attempting to find a suitable viscosity reduction of aged bitumen such that RAP and/or RAS can be used for new pavements. In addition, products from other industries, such as crumb rubber from used tyres and extenders from recycled vacuum-refined motor oil, have also been used to modify bitumen. Such additives have not yet been proven successful in extending pavement life.

Any environmental hazard or risk transferred to the bitumen product using additives or modifiers should be identified, including for recycling materials.

4.1 Bitumen emulsion

To produce bitumen emulsion, liquid bitumen is dispersed in water containing surfactants, typically using a colloid mill.

The resulting emulsion is typically 50% to 70% bitumen but can vary above or below these percentages depending on the intended usage. Emulsions consist of two phases: the dispersed phase and the continuous phase. In general terms, if the dispersed phase consists of an "oily" material and the continuous phase is aqueous the emulsion is known as an "oil in water" emulsion, sometimes denoted as "O/W". Conversely, if the continuous phase is oily and the dispersed phase is aqueous, the emulsion is known as a "water in oil" emulsion, sometimes denoted as "W/O".

The typical particle size in a bitumen emulsion tends to be in the range of 1 to 10 micrometres, depending on specific formulation and manufacturing conditions.

Although cationic surfactants are used to make emulsions that are widely used in making bitumen emulsions, anionic surfactants are also used in some regions of North America based on their performance with certain aggregate types. These are often called High Float anionic emulsions due to their gelled bitumen properties. For paving applications, most emulsions are cationic or anionic. The emulsion residue can be either a bitumen or a modified bitumen. This represents approximately 10% of global bitumen consumption.

4.2 Polymer and rubber modification

Polymer modification is a common practice in which polymers are added to bitumen for various reasons. Both natural and synthetic polymers have been used to alter bitumen properties since the early 20th century. More recently, many synthetic polymers have been utilised to enhance the properties of bitumen. Typical modifiers are:

- Natural Polymers (e.g. lignin/cellulose)
- Thermoplastics/Plastomers (e.g. polypropylene (PP), polyethylene (PE), ethylene vinyl acetate (EVA))
- Elastomers (e.g. natural rubber, synthetic rubber, polybutadiene, butyl rubber)
- Thermoplastic Elastomers (e.g. styrenic block copolymers (SB, SBS, SEBS), polyolefin blends, thermoplastic polyurethane)
- Reactive Elastomeric Terpolymers (e.g. glycidyl methacrylate copolymers)
- Ground Tyre Rubber (e.g. reclaimed scrap tyres)

Although many of the polymer types listed above are used in the modified bitumen space, elastomer polymers, such as SBS, have dominated the market for both paving and waterproofing applications.

Polymer additives generally range from 1-7% by weight of the bitumen, depending on the application, with typical levels being 3-5% by weight. Of the polymers listed above, thermoplastic elastomers account for the most extensive use of polymers in bitumen modification. These products typically stiffen bitumen at high temperatures and make bitumen more flexible at low temperatures, therefore giving bitumen the best blend of properties to address desired performance characteristics depending on end use. Crosslinked polymer-modified bitumen is produced by chemically crosslinking bitumen and polymers to obtain a three-dimensional polymer bitumen matrix and a homogenous microstructure.

Ground tyre rubber, also known as crumb rubber, has been used regionally for approximately 40 years to modify bitumen. There are two methods of incorporating crumb rubber into bitumen. The dry method involves the addition of the crumb rubber at an asphalt mixing plant, while the wet method involves mixing the crumb rubber with bitumen before asphalt production. Depending on the process, 5-20% of crumb rubber can be incorporated. Efforts to eliminate stockpiles of discarded tyres have resulted in more widespread use of crumb rubber in bituminous blends.

4.3 Cut-back and fluxed bitumen

Cut-backs are bituminous products in which a percentage of the bitumen is replaced with the addition of a volatile or semi-volatile substance, such as petroleum distillates (diesel fuel, kerosene, naphtha, and others), white spirit (Stoddard solvent), or bio-oils derived from biomass materials. The term cut-back refers to the reduction in bitumen viscosity that is achieved by "cutting" the bitumen with the volatile material. Fluxed bitumen generally uses relatively non-volatile oils that soften the bitumen without increasing its volatility. Fluxed bitumen may be used directly, modified for specific applications, or blended into other feedstocks to produce a desired outcome.

4.4 Chemical modification

Chemical modification is often used to address specific performance attributes. Chemical additives include:

- Adhesion promoters (e.g. fatty amine derivatives, imidazolines)
- Surfactants, chemical lubricating additives or waxes for warm mix systems
- Phosphorous compounds (e.g. phosphorous pentoxide, polyphosphoric acid)
- Elemental sulphur
- Maleic anhydride
- Odour suppressants, scavengers, and masking agents

Chemical additives are generally utilised at levels below approximately 1% by weight of bitumen. However, dosage rates are heavily dependent on the type of modifier selected and the desired performance attributes. Chemical modification is often used in conjunction with other modification techniques to produce a synergistic effect between the modifiers or to address specific performance properties.

Elemental sulphur can be used at low concentrations (< 1% by mass) to cross-link styrene-butadiene polymers.

4.5 Fillers

The addition of special fillers or modifiers is used to improve stiffness and viscosity characteristics. Fillers include:

- Mineral fillers (e.g. limestone, fly ash and clay)
- Adhesion promoters (e.g. hydrated lime)
- Fibers (e.g. natural - cellulose, synthetic - polypropylene)
- Natural asphalts (e.g. Trinidad Lake Asphalt, Gilsonite)
- Recycled asphalt materials (e.g. recycled asphalt pavement and recycled asphalt shingles)

The dosage rate of fillers and extending agents varies widely in paving and roofing applications, depending on intended outcomes. However, many fillers do not fully incorporate or dissolve into the bitumen. When using recycled materials to improve visco-elastic performance, careful consideration of project specifications, product handling, and worker exposure is essential.

4.6 Extending and blending agents

Adding extender agents is one of the oldest methods of modifying bitumen.

- Waxes (e.g. synthetic, such as Fischer-Tropsch; natural, such as Montan; and amide derivatives, such as ethylene bis-stearamide)
- Biogenic additives (e.g. vegetable-based components)
- Vacuum Tower Asphalt Extender (VTAE)[23]

5. PHYSICAL PROPERTIES AND CHEMICAL COMPOSITION OF BITUMEN

The manufacturing processes for bitumen described in section 3 involve removing lighter components to leave behind relatively high molecular weight and low volatility compounds [24]. The resulting products have in common that they are generally solid or semi-solid materials at ambient temperature and that they soften as the temperature increases.

Bitumen's vapour pressure at ambient temperature is below the detection limit for standard instrumentation. To facilitate transportation and handling, bitumen is heated to >140°C to become liquid.

National or international specifications regulate some of the performance-related physical properties. In contrast, other properties, like specific gravity or vapour pressure, result from the manufacturing processes used to meet the performance specification.

5.1 Physical properties

Bitumen is a thermoplastic solid or semi-solid at ambient temperature, i.e. it softens as the temperature increases and hardens as the temperature decreases. At elevated temperatures, it behaves as a Newtonian fluid, the viscosity reducing with increasing temperature. Bitumen needs to be heated before it can be handled and applied.

Bitumen is also a visco-elastic material, i.e. it behaves as an elastic solid at short loading times or when cooled and as a viscous liquid at longer loading times or when heated.

Polar molecules in bitumen lead to bitumen having an affinity with aggregates, providing a material that is adhesive and also waterproof.

Bitumen is an engineered product, therefore, the product specifications focus on defining physical properties rather than chemical composition. The properties of the substances manufactured in the refinery can also be modified for specific end-uses by modifiers described in section 4.

The physical properties of the bitumen not only determine its suitability for a given application but also defines the conditions under which the product must be handled to enable it to be placed in the structure in which it is to be used.

5.1.1. Temperature susceptibility

Bitumen is a thermoplastic material that changes its physical form according to temperature. Empirical test methods such as needle penetration, ring & ball softening point and the Fraass breaking point can be used to indicate the temperature susceptibility of bitumen either by the difference between the results of the two test methods or by calculation. For example, the difference between the ring & ball softening point and the Fraass breaking point can be used to define the effective service temperature range of a bitumen and it is commonly referred to as the plasticity range. The greater the difference between the two parameters, the greater the service temperature range. The penetration index (PI) can also be used to determine the temperature susceptibility of an unmodified bitumen. This is a calculation based on the needle penetration and ring & ball softening point and was first proposed in 1936. The PI of most unmodified bitumen falls in the range of -1.5 to 0.7, with a lower value indicating a higher temperature susceptibility and a higher value indicating a lower temperature susceptibility. These methods of describing temperature susceptibility are based on classical or empirical methods and are of limited use, particularly for modified bitumen. Recent developments have focused on the use of rheological methods using, for example, Dynamic Shear Rheometry (DSR). Temperature sweeps performed in the DSR allow the determination of the relative change in complex modulus with temperature. In North America, the temperature susceptibility can be derived from the difference between the high and the low limiting Performance Graded (PG) temperature, also referred to as the Useful Temperature Interval.

It may be desirable to reduce the temperature susceptibility of a bitumen by modification or secondary processing using, for example, oxidation or air-rectification. However, oxidation generally increases low-temperature susceptibility, making the bitumen more susceptible to low-temperature cracking.

As mentioned earlier, bitumen behaves as a Newtonian fluid at higher temperatures. For storage, handling and pumpability, it is essential to select the correct temperature to keep the bitumen viscosity at the correct level without risking degradation of the product. As a general rule, bitumen should be stored at a temperature where its viscosity is approximately 100 cSt, handled at 200 cSt and pumped at a temperature where viscosity does not exceed 500 cSt. Recommended viscosity ranges for mixing and compaction depend on plant and mix design, as well as the type of bitumen used. Manufacturers can provide their own recommended ranges.

5.2 Chemical composition of bitumen

Bitumen can be described as a complex mixture of hydrocarbons containing many chemical compounds of relatively high molecular weight. There is considerable uncertainty as to the overall molecular weight distribution of bitumen. The smallest size, approximately 300 Dalton, is determined by the distillation ‘cut point’ during the manufacture of the bitumen. The largest size has not been finally concluded. Some researchers suggest that molecular weights up to 10000 Dalton are present, while others indicate that there are probably very few if any, molecules larger than 1500 Dalton in unaged bitumen [24] [25] [26] [27].

The molecules in bitumen can be grouped into four general types/fractions according to molecular weight and polarity. The classical method of separating these fractions involves column chromatography using different solvents. This method has become known as SARA fractionation as the fractions are called Saturates, Aromatics, Resins and Asphaltenes.

The molecules in bitumen are combinations of alkanes, cycloalkanes, aromatics and molecules containing sulphur, oxygen, nitrogen and certain metals [28]. A typical elemental analysis is given in Table 1.

Bitumen functionality relates to how molecules interact with each other and/or with other materials, e.g. aggregate surfaces and water. The presence of sulphur, nitrogen, oxygen and metals in some molecules makes them slightly polar. The significance of molecules containing hetero-atoms in bitumen chemistry is the ability to form molecular associations, which strongly influence the bitumen’s physical properties and performance. The components containing the heteroatoms in bitumen obtained from different crude sources can vary in content and characteristics.

Table 1. Elemental analysis of bitumen from various sources[28]

Element	Range
Carbon, %w	80.2 - 84.3
Hydrogen, %w	9.8 - 10.8
Nitrogen, %w	0.2 - 1.2
Sulphur, %w	0.9 - 6.6
Oxygen, %w	0.4 - 1.0
Nickel, ppm	10-139
Vanadium, ppm	7-1590
Iron, ppm	5-147
Manganese, ppm	0.1 - 3.7
Calcium, ppm	1-335
Magnesium, ppm	1-134
Sodium, ppm	6-159

5.3 Chemical characterisation of bitumen

Bitumen is a visco-elastic material; therefore, chemical polarity is an important property to measure. The most polar components create interactions which give bitumen structural properties at high temperature. Whereas the least polar components give bitumen its flexibility and low temperature properties. The intermediate polarity components present in bitumen act as a bridge between the least and most polar components, making them compatible with each other.

There are several methods available for separation of bitumen into these four fractions; and therefore, naming of the fractions, which is not descriptive of the chemical composition, may vary.

When bitumen is further processed, such as in air-rectification and oxidation, the SARA analysis shows that resins are converted to asphaltenes and aromatics are converted to resins. Overall, the aged bitumen becomes stiffer and more elastic compared to the unaged bitumen. A general description of the four components is shown in Table 2.

During oxidation, the primary oxidative process is carbon-carbon bond formation via oxidative condensation. Asphaltene content is increased, while the content of naphthenic and polar aromatics is decreased [16] [17] [29]. As the asphaltene concentration increases beyond a certain point, the ambient temperature flow properties of the modified bitumen product change from visco-elastic to nearly pure elastic behaviour at ambient temperature.

The oxygen that is added to the bitumen in the air-blowing process appears to reside in hydroxyl, peroxide, and carbonyl functional groups (ketones, acids, acid anhydrides, and esters) [30] [31] [32]. Small amounts of volatile components of the bitumen are also removed during the oxidation process [19] [33]. As a result of these reactions, the PAH content of the bitumen is reduced[22] [34].

Table 2. General Description of the SARA Fractions.

Bitumen Molecular Component	Viscosity	Molecular size	Oxidation Stability	Solvency & flow	HTC High-Temperature Compliance	LTC Low-Temperature Complianc
Saturates (normal & iso-Paraffin & Naphthenic)	Low	Low	Excellent	Good	Poor	Excellent
Aromatics (Naphthenic aromatics)	Medium	Medium	Poor/ Good	Excellent	Medium	Good
Resin (Polycyclic Aromatics)	Medium to High	Medium to High	Very Poor	Poor/ Good	Good	Poor
Asphaltenes (hetero-atoms)	Very High	Very High	Poor	None	Excellent	Poor

5.4 Polycyclic aromatic hydrocarbons in bitumen

PAHs are noteworthy because of their association with health effects. PAHs are a subset of a broader group of polycyclic aromatic compounds (PACs), which may also contain other atoms, such as sulphur, oxygen and nitrogen.

Crude oils contain low levels of PAHs, which partly end up in bitumen at very low ppm levels [35]. The maximum temperatures involved in the production of bitumen, <385°C (725°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) [36]. The principal refinery process used for the manufacture of bitumen, vacuum distillation, removes the majority of PAHs. As noted above, oxidation has also been shown to reduce overall concentrations of PAHs in bitumen [22] [34]. The levels of some commonly measured PAHs in various bitumen are shown in Table 3.

Table 3. PAH content of bitumen

Polycyclic Aromatic Hydrocarbons (PAH)	PAH in Bitumen (ppm) [37] [38] [39] [40]
Naphthalene	2.5 - 3.0
Acenaphthene	BDL - 0.7
Fluorene	0.3 - 0.5
Phenanthrene	0.3 - 7.3
Anthracene	BDL - 2.0
Fluoranthene	BDL - 2.0
Pyrene	0.2 - 8.3
Chrysene	<0.1 – 11
Benzo[a]anthracene	BDL - 3.3
Perylene	BDL – 39
Benzofluoranthenes	BDL - 1.2
Benzo[e]pyrene	<0.1 - 13
Benzo[a]pyrene	BDL - 4.6
Dibenzanthracenes	BDL - 3.3
Indeno[1,2,3-cd]pyrene	BDL - 2.4
Benzo(ghi)perylene	<0.1 - 4.6
Anthanthrene	BDL - 0.1
Dibenzo[a,l]pyrene	BDL - <0.6
Dibenzo[a,i]pyrene	BDL - <0.6
Coronene	BDL - 1.9

BDL = Below Detection Limit

6. BITUMEN EMISSIONS TO AIR

Numerous studies have been conducted to characterise emissions of bitumen to air.

The bitumen manufacturing process removes the lower boiling molecules, leaving only trace emissions trapped in the bitumen.

Emissions from bitumen to air are discussed under different conditions: emissions at ambient temperatures [6.1] and emissions at elevated temperatures [6.2].

Bitumen emissions at ambient temperature are negligible. The physical properties of bitumen require that handling and application is typically carried out at elevated temperatures. Under these conditions, emissions from bitumen can occur.

Bitumen emissions in the air are a complex mixture of predominantly hydrocarbons with a broad boiling point range, typically between 150-300°C. The molecular composition can include hydrocarbons covering the range from carbon numbers >C6 through to long-branched chain aliphatic hydrocarbons, cycloalkanes and aromatics. Naphthalene derivatives are some of many compounds detected in these emissions.

Figure 7 illustrates the emission from heated bitumen in dynamic equilibrium. This figure illustrates terms often used regarding emissions from hot bitumen. Traditionally, bitumen emission is the material measured and reported to reflect the level of potential occupational exposure.

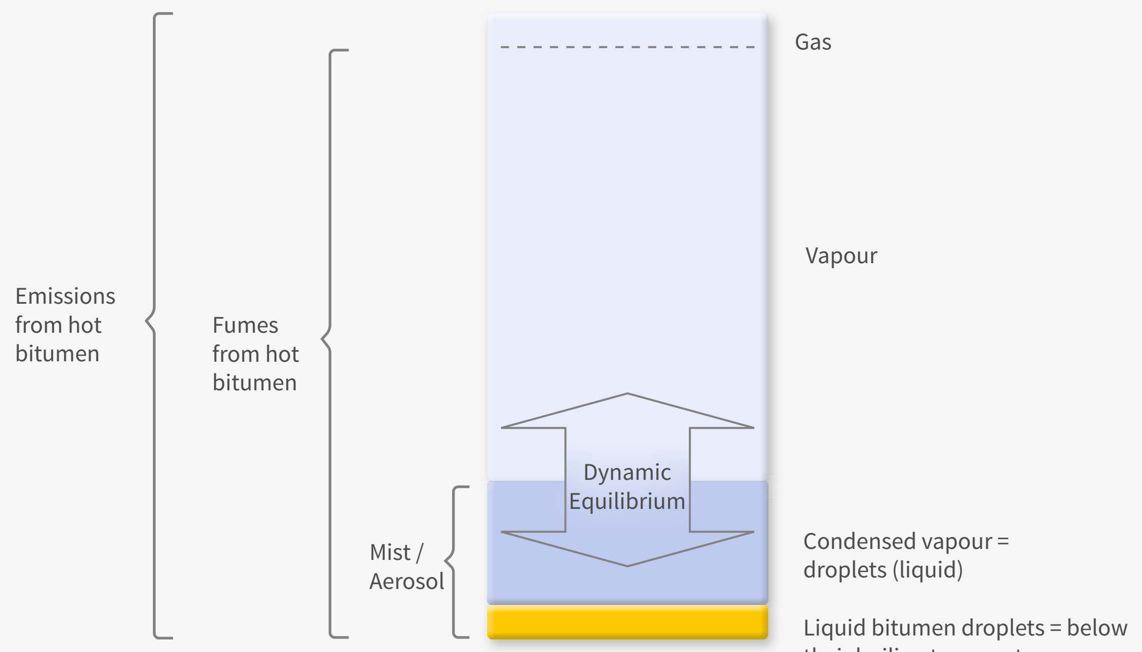

Figure 7. Schematic diagram of bitumen emissions

Gas molecules and liquid bitumen droplets are typically a minor proportion of the emissions from hot bitumen. The aerosol/mist to vapour ratio varies with ambient and operating conditions. Typically, the aerosol-to-vapour ratio is in the range 5:95-15:85, depending on the sampling method, but it should be recognised that under certain conditions, such as elevated temperature, the actual ratio encountered at workplaces may vary outside this range [41] [42]. In this document, the preferred term is bitumen emissions, which includes gas phase, vapour and aerosols, as shown in Figure 7.

6.1 Bitumen emissions to air at ambient temperatures

Historically, it was generally believed that measurable bitumen emissions only occurred during elevated temperatures when paving and roofing were applied. After cooling to ambient temperature, the emissions were considered negligible. In 2020, Khare et al. reported "Asphalt-related emissions are a major missing nontraditional source of secondary organic aerosol precursors" [43]. This laboratory study, which used a relatively small amount of bitumen (~100-200mg) to model emissions in Southern California, estimated significant emissions. To better understand the work of Khare et al., a study was conducted by Kriech et al. and published in 2022. It was titled "Characterizing Asphalt Emissions under In-Service Conditions" [44].

The Kriech study investigated emissions from thin films of bitumen under both dark and simulated sunlight conditions at temperatures ranging from 25-60°C. Film thickness was varied, and emissions were measured for 10-21 days. The impact of ageing through the hot mix asphalt plant, as well as in-service ageing, was studied. The study then looked at asphalt pavements, both newly constructed and a 17-year-old pavement, to measure emissions.

The study found that the magnitude of emissions scaled with the inverse of viscosity, whereas the composition of emissions varied with film thickness and age of the bitumen binder sample [44]. The bitumen binder exposed to solar irradiance showed short-term impacts on emissions in the first hours of exposure. Compacted asphalt pavements were used to simulate real-world, in-service conditions. The emissions from a freshly compacted asphalt pavement were compared to a 17-year-old pavement sample collected from the field to determine how the age of an asphalt mixture influenced emissions over 17 years. An increase in the complexity of the pavement system caused a slowing in the total emissions profile. The composition of emissions indicated that smaller and more volatile compounds can be released from deeper within the compacted pavement pores. In contrast, the larger and less volatile compounds remain trapped throughout the pavement's lifetime.

The most significant finding was that emissions cannot be estimated as a function of the total bitumen as Khare et al. proposed [44]. Rather, emissions are impacted by oxidative ageing, which increases the binder's viscosity, significantly slowing emissions over time. Additionally, compacted asphalt pavements are more complex than bitumen films because they are impacted by aggregate packing and the resulting protection from direct sunlight beyond the top 8-14 microns of the surface film by aggregate. In the case of pavements, the emissions are driven more by surface area than the total binder present in the pavement. The estimates from this laboratory study suggest that emissions from pavements are small (compared to emissions from vehicles) under elevated pavement temperatures and in the presence of sunlight.

The above studies did not consider the diurnal impacts of daylight and darkness as well as average temperatures and sunlight exposure throughout a year, which would further reduce estimated emissions under in-service conditions.

6.2 Bitumen emissions to air at elevated temperatures

Bitumen emissions are created when bitumen is heated to elevated temperatures. This heating lowers the viscosity of the bitumen which allows the bitumen to behave as a viscous liquid for storage, transporting, pumping and use in various applications such as manufacturing roofing materials, waterproofing, and paving applications. Depending on the grade of the bitumen, it may be heated to higher or lower temperatures. The maximum safe handling temperature for bitumen used for paving applications is 200°C, while for oxidised bitumen used in other applications it is 230°C [2].

6.2.1 Temperature effect of bitumen emissions during handling

During the handling of bitumen, or bitumen-containing materials, at elevated temperatures, small quantities of hydrocarbon are emitted. The emissions were found to be temperature-dependent. In a laboratory study, the emission rate of the Benzene Soluble Fraction (BSF) increased by a factor of 2 for about every 11- 12.5°C temperature increase in the temperature range relevant for paving applications of 140-190°C and for every 14-17°C in the temperature range relevant for roofing applications [35] [45]. Eurobitume conducted a laboratory study to compare bitumen emissions at various temperatures to avoid confounders seen in the field [46]. Although these laboratory-generated emissions showed differences using different laboratory rigs and actual worker exposures, this study design provided a way to control for confounders found in the field to examine their influence.

The test material was an air-rectified 50/70 bitumen, similar to the bitumen used in the Fraunhofer inhalation study [47]. The same source of bitumen was used for each generation, which was heated to pre-determined target temperatures of 155°C, 180°C, 200°C, 230°C, 250°C and 300°C.

Results from this study showed that as the temperature increased, the concentration of emissions released also increased. This increase in emissions produced as a function of temperature appears to correlate logarithmically, as shown in Figure 8.

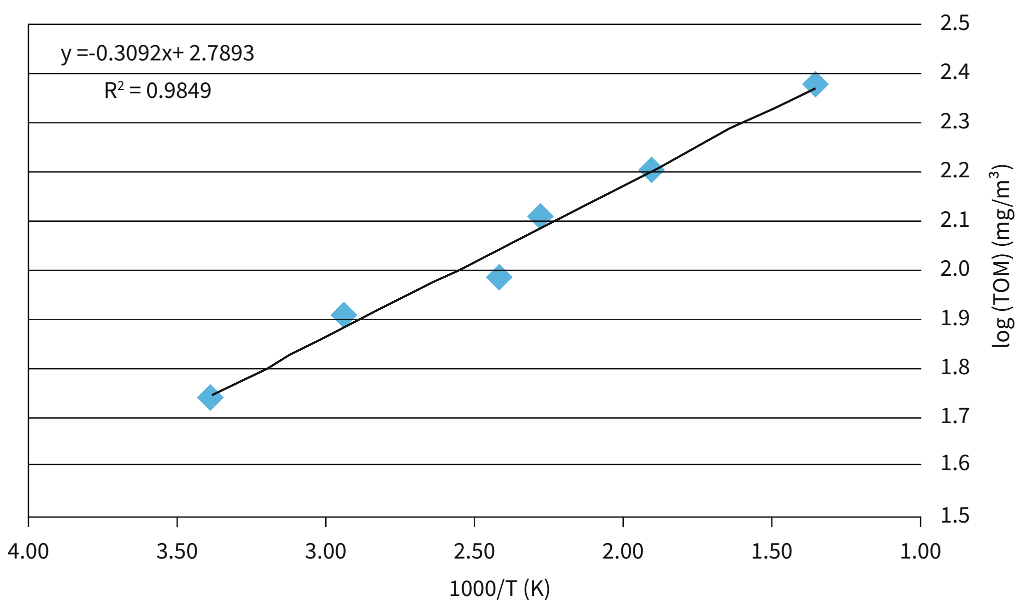

Figure 8. Log of total organic matter (TOM) (mg/m^3) as a function of the reciprocal generation temperature 1000/T (K)

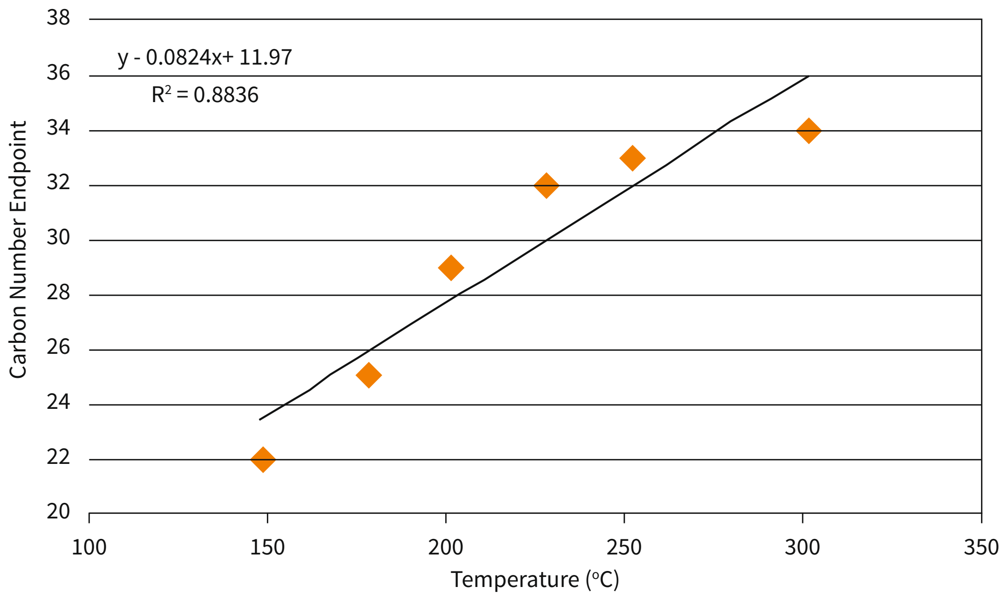

Figure 9. Fume generation temperature versus carbon number endpoint

An increase in fume generation temperature led to an increase in the boiling point distribution of the emissions and a corresponding increase in higher molecular weight compounds. The concentration of 4-6 ring PACs increased with increasing fume generation temperature. At the same time, there was a decrease in concentration of the lower molecular weight (2-3 ring PACs).

At the 155°C generation temperature, the testing showed peaks up to a carbon number of ~C22. As the fume generation temperature increased up to 300°C, the peaks detected in the chromatograms showed increasing boiling points up to a carbon number of ~C34, as graphically displayed in Figure 9 [(47)].

In summary, for the bitumen tested, an increase in the fume generation temperature led to a positive correlation between the amount of emissions and the relative quantity of higher molecular weight substances released.

In Europe, the handling of straight-run and air-rectified bitumen above 200°C and oxidised bitumen above 230°C is registered as a "condition of use advised against" under REACH.

6.2.2 Comparison of air-rectified to straight-run vacuum distilled bitumen emissions

The composition of emissions from two commercial bitumen samples have been compared. These samples were produced by the same refinery from the same crude oil but differed slightly in their processing. One bitumen was a 70/100 paving grade bitumen produced by vacuum distillation direct to grade. The second bitumen was a 50/70 paving grade bitumen produced by air-rectification. The bitumen samples were produced in the same refinery as the bitumen used in the Fraunhofer-ITEM 24-month cancer inhalation study on rats. An analytical comparison of the bitumen and laboratory-generated emissions was conducted under identical conditions [(45)]. The fume generation and analysis were carried out at Heritage Research Group, USA, on behalf of Eurobitume [(45)].

Emissions from the bitumen were generated in the "Heritage fume generator" at a temperature of 155°C, collected and extensively analysed to assess similarities and differences.

The emissions collected on the filter and sorbent tube were eluted, combined, and analysed for boiling point distribution (by simulated distillation), carbon number, and Total Organic Matter (TOM). To investigate compounds of regulatory concern, the emissions were analysed for 33 PACs covering the US EPA, and EPCRA[48]. Gas Chromatography-Mass Spectrometry (GC/MS) was used to create fingerprints of extracted compounds to further characterise compounds in the bitumen emissions.

A comparison of the emissions from the two bitumen samples led to the following conclusions:

- The boiling point distribution of both fume condensate samples was almost identical (see Figure 10);
- Similar ratios of semi-volatile to aerosol fractions were observed;
- Similar concentrations of PACs were found in both emission samples; and
- Both emission samples' GC/MS fingerprints were similar in terms of compounds identified.

Although some minor data variations are apparent, in general, the emissions generated from these two bitumen materials appear similar in composition and physical properties. Based on these results it is concluded that the results from the air-rectified bitumen used in the Fraunhofer study can be used to 'cross-read' to similar vacuum residue and straight-run paving grade bitumen [CAS# 64741-56-6] and [CAS# 8052-42-4].

6.3 Occupational exposure from bitumen emissions

Bitumen emissions can contain small quantities of compounds that regulatory agencies have classified as carcinogens or irritants. Research conducted by Eurobitume and presented in Figure 10 has shown that the quantity of emissions from bitumen is related to the temperature of the bitumen[46]. As the temperature increases, the emissions also increase and can increase occupational exposure to bitumen emissions. Thus, temperature is a crucial determinant for bitumen occupational exposure and therefore, products containing bitumen should be handled and applied at the lowest practical temperature.

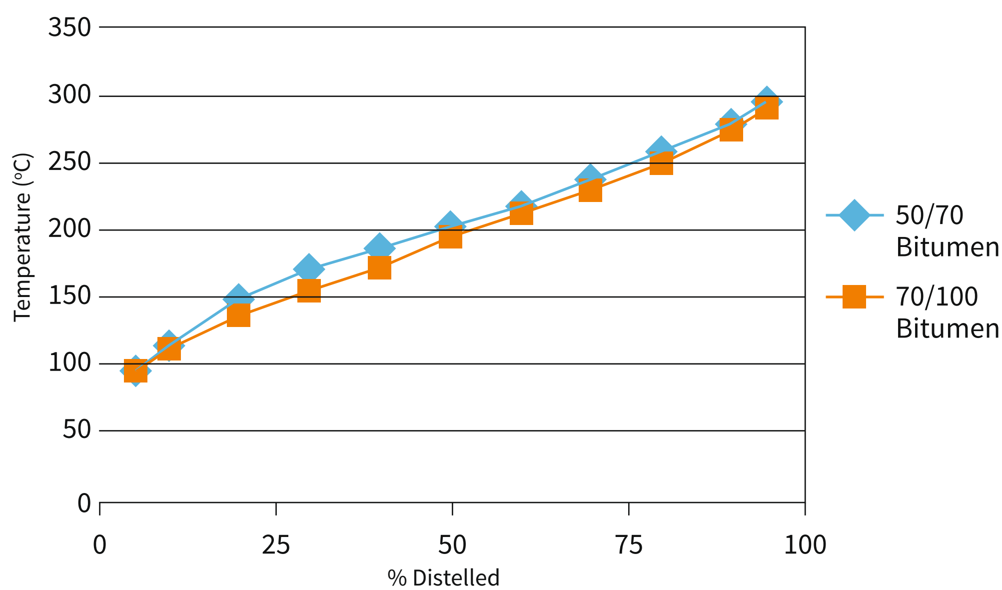

Figure 10. Boiling point distribution curves for bitumen emission samples - 50/70 (blue) 70/100 (orange).

Measuring exposure to bitumen emissions has continued to evolve with time. Historically, exposure was more related to collecting particulate matter — such as dust and aerosol found in the workplace — on filters. As time passed, the focus shifted to compounds that caused irritation, such as organic matter captured on the filter or passed through the filter to be collected on a sorbent media. In more recent years, the focus has shifted to measuring compounds that could be potential carcinogens. To understand exposure over time, it is important to use the same methods with the same endpoints to make a proper comparison.

Two significant studies examined asphalt emission exposures over time [(49) (50)]. Both studies found that worker exposure to bitumen emissions has reduced substantially. Using multi-centre occupational cohort study results, Burstyn et al., modelled that worker exposures decreased by a factor of two to three every ten years based on time trends from multivariate statistical models [(49)]. Numerically, the model predicted a decrease from 1.2-2 mg/m^3 (1960) to 0.2-0.5 mg/m^3(mid-1990s) as shown in Figure 11. After a temporary increase when recycling old asphalt contaminated with coal-tar-containing layers in Europe, exposures show a steady decrease since the mid-1970s. This coincides with the banning of hot-recycling of coal-tar-containing layers. This study also modelled trends for organic vapour and benzo[a]pyrene. Reduction of handling and application temperatures, safe handling education, use of engineering controls, and alternative cleaning products are some of the factors involved in reducing worker exposures. Since then, other developments, such as warm mix asphalt, have contributed to further exposure reduction.

As testing continued globally, various methodologies and test protocols were applied in individual studies, limiting the comparability of data.

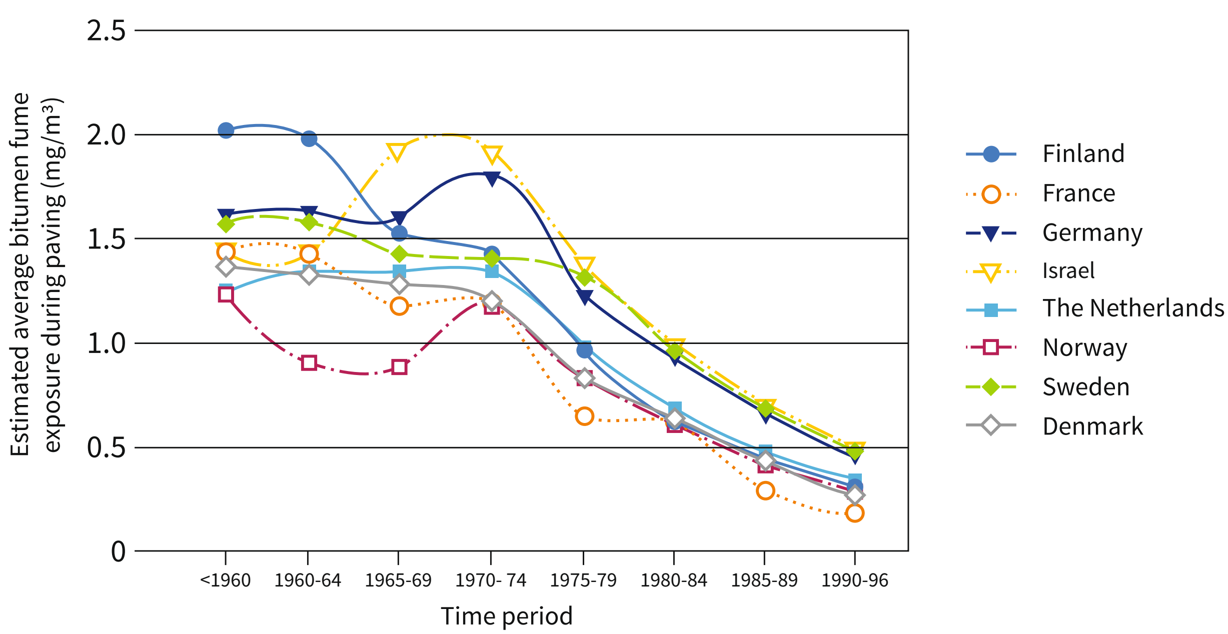

Figure 11. Assessed time trend in average exposure to bitumen emissions (pavers only)[(49)].

Similarly, in roofing plants, Fayerweather shows a sharp reduction in bitumen emission exposures over time due to the addition of emission control devices, the switch from organic felt to glass mat as the core of the shingle, and a general reduction in bitumen temperatures used in manufacturing [50]. Total particulates and the corresponding benzene soluble fraction have decreased more than 11-fold since 1977-79 in roofing plants in the study.

6.3.1 Studies on occupational exposure from bitumen emissions

6.3.1.1 Irritation studies on bitumen emissions
Several components of emissions from hot bitumen, including hydrogen sulphide (H_2S) (see also section 6.3.3), have been associated with eye, skin, and/or respiratory irritation, as summarised by NIOSH and ACGIH [51] [52]. Heating bitumen increases emissions that can be inhaled or come into contact with the skin. Keeping the temperature of heated bitumen as low as possible is an important way to reduce the generation of bitumen emissions, lowering the potential for irritation. Additional engineering controls and work practices should also be adopted.

A number of studies have been conducted on the potentially irritating effects of bitumen emissions on the skin, eyes and lungs of asphalt and bitumen workers. A 1991 paper by Norseth et al. investigated irritation symptoms in Norwegian asphalt workers [53]. The study found higher reported irritation in asphalt workers compared to a control group of road maintenance workers not exposed. The study found that high levels of trimethylbenzene compounds may be responsible, specifically 1,2,4- trimethylbenzene. In a collaborative study by Norseth and Heritage Research Group, a study of potential sources of 1,2,4-trimethylbenzene was investigated in asphalt workers in the US at 11 asphalt paving sites [54]. The study found that unmodified asphalt emissions tended to be low in 1,2,4-trimethylbenzene, but a small amount of diesel oil (then widely used for cleaning tools on paving crews) produced higher levels (1100% compared to bitumen not contaminated with diesel oil) in the breathing zone. This led to increased use of alternative cleaning agents.

In 1999, Gamble et al. studied asphalt workers looking at short-term lung function impacts from exposure to asphalt paving emissions [55]. In this study, five different segments of the bitumen industry in the US participated in exposure monitoring, symptom surveys of irritation, and lung function testing over two days for each worker. The study could not find a correlation between exposure, symptoms, and lung function changes.

In 2000, Ma et al. conducted a study on the impact of bitumen emissions on rat lungs both in vitro and in vivo and found bitumen emission condensates do not cause significant pulmonary inflammation or lung damage [56].
In 2004, Randem and in 2007 Ulvestad studied Norwegian asphalt workers for lung function decline [57] [58] [59]. In both studies, there was a seasonal decline in lung function. These studies measured many parameters of exposure. Since this study was in direct contrast to Gamble´s and Ma´s studies, the industry investigated potential differences between exposures in Norway and the US. Norway has mostly high silica aggregates compared to the US. It was found that amine adhesion agents are widely used in paving materials. The Safety Data Sheets (SDSs) indicate that these aliphatic amines may cause chronic allergic respiratory reactions in individuals and may have played a role in the differences in outcome between the two studies. None of the studies except Gamble controlled for confounding irritating effects, such as diesel oil used for cleaning tools and equipment and adhesion agents in the bitumen.

Ramboll Environ researched whether hot mix asphalt paving is associated with decreased lung function or obstructive lung disease. To meet this objective, Ramboll Environ performed a systematic review and synthesis of the epidemiological literature. After completing this research, the authors concluded “Clear, consistent, and unbiased evidence of an association between hot mix asphalt exposure and lung function or obstructive lung disease was not after found.” Regardless of the reported outcomes, much of the literature had significant limitations, and therefore, the evidence was inadequate to support a causal conclusion (60).

6.3.1.2 Cancer studies on bitumen emissions
Bitumen contains trace levels of 4-6 ring PACs (Polycyclic Aromatic Compounds), some of which are of concern due to their carcinogenic nature. Animal testing of un-modified bitumen has found bitumen not to be carcinogenic due to the fact that the PACs are not bioavailable, they remain trapped within the bitumen matrix (61). However, these trace PACs can be volatilized and concentrated in the resulting emissions when heated. Because of their high boiling point and low vapour pressure, the 4-6 ring PACs tend never to be released when bitumen is heated below 200°C. However, 2-3 ring PACs, which are not carcinogenic, can be emitted at temperatures below 200°C.

IARC made the following statement in Monograph 103: *“Results of studies with condensates generated at > 199°C strongly suggest that temperature plays an important role in determining the degree of exposure and also the carcinogenic potential of bitumen emissions”* (62). This statement was supported by two papers that were part of a more extensive animal skin painting study. The first, titled “Generation of Bitumen Fumes Using Two Fume Generation Protocols and Comparison to Worker Industrial Hygiene Exposures”, involved testing and collecting emissions from four paving bitumen used at <150°C and four roofing bitumen used at >200°C (63). In the follow- up study, animal skin painting studies used one roofing and one paving fume condensate selected by a nine-member US Scientific Advisory committee consisting of government, academia and private consulting (64). The fume condensates from paving bitumen that was matched to paving worker exposures did not produce tumours in lifetime animal skin painting studies. However, fume condensates from roofing applications heated to >200°C did produce a weak cancer response in animals.

A third animal inhalation study conducted by the Fraunhofer Institute on European paving bitumen emission condensates collected at ~150°C matched to worker exposures also showed no cancer in animals (65). A 2015 study by Bolliet found that 4-6 ring PACs increase in concentration in emission with increased temperature. The study stated: *“At 200°C and below, concentrations of 4-6 ring PACs were ≤6.51 ≤ g/m^3 for all test materials, even when flux oil was used. Trends in temperature-process relationships from this study can be used to guide industry decisions to reduce worker exposure during processing and application of hot bitumen”* (66).

As reviewed in the prior sections, crude oil contains polycyclic aromatic compounds, some of which are carcinogenic. While most PACs segregate into other petroleum streams during refining, relatively low concentrations of residual PACs can be present in bitumen. As a result, bitumen has been studied for cancer potential.

Published data suggests that unmodified bitumen does not present a cancer hazard (61). The low levels of PAHs in bitumen are not readily bioavailable through inhalation, and human exposure to PAHs from handling the bitumen substance is very low. The principal occupational exposure during the handling and application of hot bitumen is due to its emissions.

A review of cancer potential in humans from occupational exposure to bitumen & bitumen emissions was conducted by the International Agency for Research on Cancer (IARC) in 2011 and published in 2013 [62]. The overall evaluation of cancer potential in humans was based on consideration of cancer findings in humans, cancer studies in experimental animals, and mechanistic and other relevant data. In that review, IARC noted the potential influence of solvents and temperature on carcinogenic potential.

IARC observed that there were no consistent increases in cancer in either the occupation of paving or in animal studies with paving bitumen or emissions (see also Clark et al., 2011)[64]. Limited evidence was observed for cancer associated with the occupations of roofing and mastic asphalt. No animal data is available for mastic asphalts. Animal studies of Asphalt Fume Condensate (AFC) from a specific type of roofing bitumen, Type III Built-Up Roofing Asphalt (BURA), resulted in evidence of cancer potential in mouse skin [64] [67].

The IARC evaluation of the "mechanistic and other relevant data" concluded that there was 'strong' evidence for a mechanism for cancer in the occupation of paving, which was of sufficient importance to elevate the overall conclusion for paving from Category 3 to Category 2B. The mechanistic evidence for the roofing and mastic sectors was considered weak; hence, this had no bearing on the final evaluations for these sectors. The overall conclusions are summarised in Table 4.

Table 4. Summary of IARC Evaluation[62]

Occupational Sector	Bitumen Type/Class	Overall Evaluation
Paving	Straight-run bitumens	Occupational exposures to straight-run bitumens and their emissions during road paving are possibly carcinogenic to humans (Group 2B)
Roofing	Oxidised bitumens	Occupational exposures to oxidised bitumens and their emissions during roofing are probably carcinogenic to humans (Group 2A)
Mastic	Hard bitumens	Occupational exposures to hard bitumens and their emissions during mastic-asphalt work are possibly carcinogenic to humans (Group 2B)

In 2018, a paper titled "Assessing cancer hazards of bitumen emissions – a case study for complex petroleum substances" was published [68]. This paper examines the difficulties in identifying cancer hazards associated with complex substances such as bitumen emissions. There are frequently contradictory findings across human, animal, and mechanistic studies. Additionally, it is important to incorporate a validation step that matches real-world exposures, and to control for confounding factors in study design so that necessary read-across can be made during assessments. Several key studies on bitumen emissions in two-year dermal cancer assays reported variable outcomes ranging from high cancer incidence to no cancer incidence. The paper synthesised findings from published studies to explain the differences and discuss critical factors in cancer hazard evaluation for complex petroleum substances. Using these vital factors, the study reviewed relevant human genetic toxicity, mammalian toxicity and mechanistic studies of bitumen to understand the divergence in results. The paper assessed the most reliable and scientifically supported information on the potential carcinogenic hazards of bitumen emissions and commented on the quality and completeness of data. Human exposure data are typically considered the highest priority because they eliminate the need for interspecies extrapolation and reduce the range of high- to low-dose extrapolation during the risk assessment. Two comprehensive animal studies were also discussed, which allow for effective read-across from human, animal and mechanistic components, control confounders, and are well-validated analytically against workplace exposures. These studies provide the strongest evidence base for evaluating cancer hazards.

Ramboll Environ conducted a meta-analysis to assess if there are any cancer risks from exposure to bitumen and bitumen emissions. Their paper "Cancer Risk Associated with Exposure to Bitumen and Bitumen Fumes: An Updated Systematic Review and Meta-Analysis" evaluated whether cancer risks are increased among bitumen (asphalt) workers. The analysis showed lung cancer risks were not increased among bitumen-exposed workers [69].

Gradient's work on the Quantitative Risk Assessment (QRA) for paving grade asphalt was published in the journal "Critical Reviews in Toxicology" [70]. Gradient is an environmental and risk sciences consulting firm renowned for specialising in Toxicology, Epidemiology, and Risk Assessment. This published paper complements the QRA that Gradient conducted for BURA, which was published in 2015 [71]. These papers show very low risks for workers for both dermal and inhalation exposures.
In March 2020, the German Technical Rules for Hazardous Substances (TRGS) 905 List of carcinogenic, mutagenic or reprotoxic substances was updated [72]. The following substance was added as probably carcinogenic: oxidised bitumen: vapour and aerosol during the hot processing of oxidised bitumen.

6.3.2 Inhalation exposure measurement

Occupational exposure to bitumen emissions is measured using a personal monitoring sampler. The collection of static (area) or environmental samples does not provide a reliable indication of personal exposure. The type of sampler used and the method by which the collected emissions are analysed can lead to substantial differences between measured values [73].
When comparing results of personal exposure monitoring surveys, it is essential to take into account the method used and the metric being employed. Exposure monitoring methods for bitumen emissions fall into three main categories that measure:
1) particulate matter,
2) solvent-soluble fraction of particulate matter, and
3) organic matter.

For the categories listed in 6.3.2.1 to 6.3.2.3, there are numerous variables, all of which may influence the measured values;

- type of sampler (e.g. open face, closed face, inhalable particulate),
- type of solvent used to extract the filter (e.g. cyclohexane, benzene, dichloromethane),
- type and quantity of sorbent used to capture the vapour phase (XAD-2), Tenax®, activated, coconut charcoal, or a combination),
- duration of sampling,
- analytical method,
- flow rate of air through the filter.

The resulting differences make it difficult, if not impossible, to directly compare measurements taken using different methods [74] [75]. Many countries use gas chromatography with flame ionisation detection (GC/FID) to determine the TOM/THC. On the other hand, Germany uses Fourier transform infrared (FTIR) analysis. TOM fractions have also been analysed using fluorescence spectroscopy.

NIOSH Method 5800 fourth edition measures total concentrations of PACs in bitumen emissions using an ultraviolet fluorescence technique in their Health Hazard Evaluation Report (76) (77). Osborn et al. developed a fluorescence technique to maximise the response to 4-6 ring PACs that may be present in bitumen emissions; this screening method has been used in many industry studies (78) (79) (80) (81) (82) (83).

6.3.2.1 Particulate matter

Total Particulate Matter (TPM) 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. NIOSH Method 5042 refers to this measure as total particulates (TP) (84). It represents the nonspecific gravimetric amount of organic and inorganic particles quantifying the total dust collected onto the filter that passes through the 4mm inlet of the sample cassette. Sampling differences primarily involve filter type and inlet opening size affecting face and capture velocity.

6.3.2.2 Solvent soluble fraction of particulate matter

Benzene Soluble Matter/Fraction (BSM/BSF) (or Cyclohexane Soluble Matter/Fraction (CSM/CSF): these methods rely on a collection of the particulate fraction as described above. However, 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 emissions), although this gravimetric measure is also nonspecific and does not differentiate between sources of exposure. Sampling differences here include collection medium, solvent purity, and ability of the selected solvent to solubilize bitumen emissions. Due to its carcinogenicity, benzene is not used as an extraction solvent in many countries.

A sub-set of such methods uses a special monitoring aerosol sampler to collect only a specific fraction of the particulate matter, e.g. the respirable, thoracic or inhalable fractions (85).

6.3.2.3 Organic matter

Total Organic Matter/Total Hydrocarbon (TOM/THC) is the sum of the organic part soluble fraction of particulate matter plus the organic vapour phase collected using a backup sorbent.

In addition to monitoring exposure to bitumen emissions, some studies have evaluated exposure to individual or groups of PAHs or PACs as components of bitumen emissions (63) (79) (81) (86) (87). A number of different lists of PAHs are used because different researchers, regulators and advisory bodies have their views of which substances should be regarded as potentially hazardous. Due to the complexity of bitumen emissions, with instrumentation advances, GC/MS is recommended over high-performance liquid chromatography (HPLC) since similar detection is achievable with greater resolution and mass spectral confirmation (88).

It should be recognised that none of the methods of measuring exposure are bitumen-specific but will capture particulate and vapour fractions of all 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. Complications with worker exposures in real-world environments can be better understood with the aid of chromatographic methods such as GC/FID. However, quantification of these confounders can be challenging to isolate.

6.3.3 Dermal exposure measurement

At ambient temperatures, bitumen is solid or semi-solid. Apart from physical abrasion, skin contact with solid bitumen is not expected to cause health effects. If hot bitumen comes into contact with the skin, severe thermal burns can result. Cut-back, fluxed and emulsified bitumen products (see section 4.3) are usually handled at lower temperature, so the risk of burns is significantly reduced. The diluent, however, can allow certain compounds in the bitumen to enter the dermal layers.

Dermal monitoring techniques are varied, and no standardised approach is used by researchers [89]. Specific to bitumen workers, a variety of dermal techniques have been used. Väänänen et al. used hand wipes with sunflower oil and polypropylene pads [90]. McClean et al. used polypropylene filters attached to an exposure pad [91]. Due to limitations in the range of compounds collected, retained and recovered from existing surrogate skin samplers, Olsen et al. developed a 5-layer passive organic dermal (POD) sampler [92]. Samplers, dermal collection sites, extraction, and analytical methods are all varied, making it difficult to compare results.

Traditionally, exposure monitoring has focused on inhalation as the primary route of exposure. However, the possibility of dermal exposure and uptake of components of bitumen emissions, arising from dermal contact with condensed fumes/emissions has been considered in recent years. This section covers studies of dermal exposure to bitumen emissions. Other documents detail exposure to bitumen during handling and application of materials containing bitumen during paving, roofing and mastic asphalt operations [3] [5] [4].

As part of a multi-country nested case-control study on lung cancer risk among asphalt workers, Boffetta et al. included an assessment of dermal exposure to bitumen fume condensate using the DREAM methodology [93] [94]. 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 [95]. Using polypropylene exposure pads, Fustinoni et al. studied dermal exposures to 24 bitumen workers, with samples collected at the neck, shoulder, upper arm, wrist, thigh close to the groin, and the outer side of the ankle [96]. Of these locations, the wrist showed the highest sum of PAH contamination with phenanthrene [CAS# 85-01-8] present in all samples.

Cavallari et al. studied dermal exposures measured under three scenarios using POD samplers and hand wash samples; all were low, with most samples for each analyte being below the limit of the detection except for phenanthrene and pyrene [97]. The geometric mean concentrations for phenanthrene and pyrene were 0.69 ng/cm^2 and 0.30 ng/cm^2 respectively, on the polypropylene layer of the POD samplers and 1.37 ng/cm^2 and 0.29 ng/cm^2 respectively in the hand wash samples. In line with the research by Boffetta et al. mentioned earlier, Cavallari et al. showed that using gloves more frequently was associated with a notable reduction in exposure to specific chemicals based on hand-washing samples collected. Predictive models indicate that switching to bio-based cleaning agents instead of diesel, regularly wearing gloves, and reducing the temperature when handling certain materials could decrease skin exposure by 76-86%.

6.3.4 Urinary biomarkers of polycyclic aromatic compound exposure

Biological markers (biomarkers) have been used to assess exposure to PACs or PAHs during occupational exposure to bitumen emissions. Although biomonitoring of exposure is a long-standing practice, complications arise due to confounders from diet and other sources on the job site. Also, when the concentrations of the pre-shift and post-shift samples differ by less than a factor of 10, interpretation of the results is sometimes difficult.

In a study with volunteers exposed to bitumen emissions 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 to indicate the 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 [(98)].

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"* [(99)].

Pesch et al. investigated biomarkers of bitumen exposure in a cross-shift study in 317 exposed and 117 non-exposed workers [(100)]. Post-shift concentrations, after statistical modelling, showed a slight increase in 1- hydroxypyrene by a factor of 1,02 per 1 mg/m^3 bitumen ($P = 0,02$) and 1,04 for 1- and 2-hydroxynaphthalene ($P < 0.001$).

McClean et al. studied personal air, hand wash and urine samples from 12 paving workers over three consecutive workdays during four workweeks [(101)]. Results provide evidence that PAHs in the air are dermally absorbed. This study also showed that reducing the application temperature of asphalt mix holds great promise for reducing PAH exposure among paving workers. To achieve further reductions, it may be necessary to increase the amount of dermal coverage for workers.

6.3.5 Hydrogen sulphide

Hydrogen sulphide (H_2S) is a colourless, naturally occurring gas contained in many of the world's crude oils. It is formed by the anaerobic degradation of organic sulfur compounds in crude oil when exposed to high temperatures or catalysts in the refining process.

H_2S is highly flammable and can react with iron oxide (rust) on the walls and ceilings of tanks to form pyrophoric iron sulphide, a known ignition source in the presence of oxygen.

H_2S is a hazardous gas that may be present in the vapour space of tanks, trucks, rail cars, and barge compartments that contain (or have contained) hot bitumen. Many factors influence the presence and/or release of H_2S in bitumen, including temperature, agitation, crude oil source, blend components, and additives (e.g. H_2S scavengers). Changing storage and handling conditions may increase or reduce the release of H_2S.

H_2S gas is toxic, acting on the nervous system, and irritating, acting on eyes and the respiratory system. Adverse effects can occur very quickly and may lead to death. It is characterised by a strong odour of "rotten eggs" at concentrations well below 1 ppm [1.4 mg/m^3] air. It is a flammable gas, heavier than the air which, when inhaled even at low concentrations, causes breathing difficulties and breathlessness accompanied by loss of sense of smell. Odour is not a reliable way to detect its presence.

H_2S usually produces no permanent effect as long as concentration levels remain low (that is, within exposure limits). H_2S effects at these levels are not cumulative and will not build up in the body. For more information on the management of H_2S risks in bitumen facilities, consult the Asphalt Institute's IS-225: "Management Practices for Asphalt Facility Control of Hydrogen Sulphide Exposure" and "Potential Risks of Hydrogen Sulphide through the Bitumen Manufacture and Delivery Process" available from Eurobitume [102] [103].

Monitoring is critical to ensure workers and the environment are protected from dangerous levels of H_2S. It is recommended that workers with a risk of being exposed to H_2S should always wear portable H_2S monitors when working around potential H_2S sources and be trained to seek safety should the monitor alarm. An electrochemical sensor is the most practical type of H_2S detector because its response time is in seconds when H_2S is present.

6.3.6 Naphthalene

Naphthalene is found at low concentrations in bitumen emissions. Naphthalene has been identified as a confirmed animal carcinogen and a possible human carcinogen under EU CLP regulations and by U.S. regulators. These conclusions were largely based on evidence of tumours in studies conducted in rats and mice. Significant additional research by the Naphthalene Research Council, including 28 peer-reviewed publications, indicates that some of the cancer data is not relevant to humans and that potency estimates are not valid. Additional research is ongoing, and a final US EPA IRIS (Integrated Risk Information System) review is expected by the end of 2024.

6.4 Refinery and terminal exposure data

Workplace exposure measurements are susceptible to variability in magnitude and potential contaminants from a variety of possible 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 the development of dose-response relationships or potential risk estimates.

A combination of published and unpublished refinery and terminal exposure data is presented in Appendix 5. Exposure data during handling and application of bituminous materials can be found in other documents devoted to the specific sectors of paving, roofing and mastic asphalt [5] [41] [51] [77] [104] [105] [106].

However, a comparison using summary information is provided in Table 5. For each sector, the worker breathing zone exposure data were summarised to provide inhalation information for TP (Total Particulate), BSF, and TOM (Total Organic Matter). Summary statistics were weighted by a number of subjects within each exposure study. Table 5 includes refinery sector data shown in Appendix 5 summarised using this approach.

Table 5 also provides inhalation data for the mastic sector, including BSF and TP results from Brandt et al. [39] and uses methods similar to the other data presented. A different method is used by BGIA in Europe (BGIA sampling system GSP (BG-Institute for Occupational Safety and Health – BGIA) with FTIR analysis). Rühl et al., using this BGIA method, provide directly comparable vapour plus aerosol data. on the following sectors: rolled paving, roofing application, and mastic asphalt [41].

Table 5. Summary estimates for various industry sectors

	Total Particulates			
	Arithmetic Mean (AM) TP mg/m^3	Geometric Mean (GM) TP mg/m^3	No. of workers represented AM/GM	Studies Represented AM (GM)
Refinery/Terminal[a]	**0.46**	**0.18**	*204*	*19*
Roofing - Manufacturing[b]	**0.84**	**0.62**	*686/821*	*3[c] (5)[d]*
Paving - Hot Application	**1.45**	**0.32**	*1896/2251*	*11g (13)h*
Roofing - Hot Application	**1.34**	**0.89**	*299*	*14[l]*
Mastic	**20.7**	**na**	*12*	*3[m]*
	Benzene Soluble Fraction			
	Arithmetic Mean BSF mg/m^3	Geometric Mean BSF mg/m^3	No. of workers represented AM/GM	Studies Represented AM (GM)
Refinery/Terminal[a]	**0.28**	**0.10**	*197*	*16*
Roofing - Manufacturing[b]	**0.22**	**0.11**	*882/1017*	*4[c] (5)[d]*
Paving - Hot Application	**0.16**	**0.09**	*749/962*	*9[i] (13)[h]*
Roofing - Hot Application	**0.77**	**0.46**	*338*	*18[m]*
Mastic	**12.8**	**na**	*12*	*3[m]*
	Total Organic Matter			
	Arithmetic Mean TOM mg/m^3	Geometric Mean TOM mg/m^3	No. of workers represented AM/GM	Studies Represented AM (GM)
Refinery/Terminal[a]	**2.43**	**1.31**	*32*	*2*
Roofing - Manufacturing[b]	**1.50**	**0.82**	*151/228*	*1[e](2)[f]*
Paving - Hot Application	**1.10**	**0.72**	*335/415*	*6[j] (5)[k]*
Roofing - Hot Application	**1.47**	**0.71**	*115*	*4[n]*
Mastic	**Range = 0.13 – 77***		**608**	*1[o]*

*vapour and aerosols (v + a) using the BGIA sampling system GSP (BG-Institute for Occupational Safety and Health – BGIA) with FTIR analysis.

Summary statistics weighted by number of subjects within each exposure study. [a] References found in Appendix 5; [b] Includes roofing asphalt manufacturing in co-located facilities; c (107); (83); (95); d (107); (83); (95); (108); (55); e (83); f (83); (55); g (95); (108); (39); (63); (82); (80); (109); (110); (111); (81); (112); h (83); (95); (108); (63); (82); (80); (109); (110); (111); (81); (112); (104); (77); i (107); (83); (63); (82); (80); (110); (111); (81); (112); j (83); (82); (80); (81); (104); (105); k (83); (55); (82); (80); (81); l (106); m (39); n (41)

6.5 Occupational exposure limits

Occupational Exposure Limits (OELs) are often set for 8 hours and for short term peaks to be representative of daily worker activities. Laboratory studies on bitumen emissions often require significant quantities of samples, which cannot be obtained easily from field activities due to the low emissions level in bitumen. The low emission level in many applications means that prolonged sampling periods are needed to collect sufficient emissions for reliable measurement. Surrogate samples can be generated using laboratory methods, which are validated to represent emissions to which workers are exposed. Such material is usually collected as condensates, combining all gaseous, vapour, aerosol, and liquid particulate fractions. Accordingly, any artificially generated emissions must be characterised and matched against emissions found in the workplace.

Bitumen fume-induced upper respiratory tract and eye irritation are the health-based endpoints used typically to establish workplace limit values for bitumen (fume), while cautionary statements concerning potential cancer hazards and/or absorption through the skin are often included as part of the exposure limit [88].

Currently, no international standardised method for sampling and measuring potential bitumen emission exposure exists. Nonetheless, OEL for bitumen emissions have been set in over 50 countries, Canadian provinces and U.S. states. Regulatory limits in different countries and voluntary guidelines developed by independent non-governmental organisations vary considerably in respect to numerical values and methods of evaluation. Appendix 3 shows examples of these limits. However, source documents should be used to obtain the latest information.

In Germany, an OEL of 1.5 mg/m^3 (IFA method 6305-2) on vapours and aerosols from handling hot straight-run or air-rectified bitumen at workplaces is listed in TRGS 900 [113]. Naphthalene is reasonably anticipated to be a human carcinogen [114]. Exposure limits include an ACGIH Threshold Limit Value-Time Weighted Average (TLV-TWA) of 10 ppm (52 mg/m^3). However, worker exposures have been shown to be orders of magnitude below this limit, with the maximum concentration at 0.014 mg/m^3 [114] Regulatory guidelines exist for hydrogen sulphide exposure (see section 6.3.5). Table 6 below shows examples of workplace H_2S exposure limits.

Table 6. Examples of workplace H_2S exposure limits

ACGIH (TLV-TWA) as an 8-hr TWA	1 ppm TWA, 5 ppm STEL (Short Term Exposure Limit)
OSHA	20 ppm STEL, 50 ppm Peak
NIOSH Recommended Exposure Limit (REL)	10 ppm STEL (15mg/m^3) as a 10-minute ceiling
SCOEL	5 ppm (8-Hour TWA), 10 ppm STEL
UK - EH40/2005 recommended an 8-hour TWA, m[115]	5 ppm (7 mg/m^3) STEL (15 min): 10 ppm (14 mg/m^3)
Germany - TRGS 900 (OEL) [113]	5 ppm, with peak limitation category I and pregnancy risk group C
EU-IOEL[106]	7 mg/mg/m^3, 5 ppm as TWA, and 14 mg/m^3, 10 ppm as STEL

7. SAFETY AND ENVIRONMENT

No safety or environmental impacts have been identified from exposure to the final, in-service use of bitumen products, e.g., pavement, roofing, etc. In addition, the properties of bitumen do not meet the criteria for classification as hazardous to health, e.g. under EU regulation on Classification, Labelling & Packaging (CLP) [107]. However, occupational exposure to bitumen and bitumen emissions may be associated with potential risks, as defined below.

A hazard is the existence of a source of potential damage, harm or adverse health effects. A hazard can exist without doing any harm.

Risk is the chance or probability that a person will be harmed or experience an adverse health effect if exposed to a hazard.

For example, IARC states that "A cancer hazard is an agent that is capable of causing cancer, whereas a cancer risk is an estimate of the probability that cancer will occur given some level of exposure to a cancer hazard" [118].

7.1 Safety

7.1.1 Burns

Contact with hot bitumen can cause severe burns to the eyes and skin, even in small quantities. Full covering clothing (i.e. flame-retardant coverall) and other Personal Protective Equipment (PPE) such as heat-resistant gloves, safety glasses, and safety helmets, with full visors and neck apron, can help to prevent burns during handling. For additional information on preventing burns, consult VA-26: Safe Handling of Hot Asphalt [119]. First Aid guidance is available through Asphalt Institute and Eurobitume [120] [121].

7.1.2 Hazard communication of additives and modifiers

Manufacturers of bitumen products should comply with hazard classification and communication regulations for the product and, as appropriate, identify any hazardous additives used in the product, in addition to any hazards or risks arising from the non-bituminous component(s). If appropriate, any risk associated with the bitumen product should be identified. The non-bitumen blend components identified in section 4 are added at varying dosage levels depending on the additive. Composition and potential exposure downstream of manufacturing operations are being addressed in documents by application sectors for paving, roofing, and mastic asphalt [3] [4] [5].

Manufacturers who produce bitumen products must comply with the regulations for hazard classification and communication of the product. They should also identify any hazardous additives present in the product along with any hazards or risks arising from its non-bituminous component(s). If necessary, the risks associated with the bitumen product should be identified as well. The non-bitumen blend components are added at varying dosage levels based on the additives used. The documents by application sectors for paving, roofing, and mastic asphalt address the composition and potential exposure downstream of manufacturing operations.

7.1.3 Classification and labelling

The industry considers bitumen to be safe when used under the appropriate safe handling guidelines. Potential hazards associated with bitumen use are not solely derived from the intrinsic properties of the bitumen itself but rather reflect use conditions. In Europe, CONCAWE publishes recommendations for the European classification and labelling of petroleum substances. According to these recommendations, bitumen is not classified as hazardous to health or the environment[122]. Similar broad industry-based health recommendations have not been specifically made in North America, where C&L decisions are solely made on a case-by-case basis by manufacturers and suppliers under U.S. OSHA and Canadian WHMIS regulations. General industry guidance for applying GHS to complex petroleum-derived substances such as bitumen can be found linked to the United Nations GHS site at: http://www.unece.org/trans/danger/publi/ghs/guidance.html.

7.1.4 Loading matrix

The Asphalt Institute and Eurobitume have produced two bitumen loading matrices. These provide helpful guidance to terminal operators to reduce/eliminate contamination of bituminous products. Additionally, it will allow terminal operators to check how well their company procedures/protocols stack up against both loading matrices. Although it is not intended to be used as a daily reference, it should catch the anomaly/exception loading scenarios to avoid the potential for fires and boil overs when the bitumen is being transported. More information can be found in Appendix 2 and on the Asphalt Institute, and Eurobitume websites.

7.2 Environment: Impacts of bitumen on water and soil

Bitumen has been used for over a century in pavements, roofing materials, and waterproofing applications worldwide. However, because bitumen is typically derived from petroleum, there are concerns about these materials' environmental and health impact.

Three published review articles summarise the past 30 years of research studying the environmental impact of bitumen on stormwater runoff and soil:

De Buyck, in 2021, looked at stormwater runoff and leaching from all roofing systems, including bitumen, metallic, wood, solar, tile, slate, single-ply, and synthetic roofing systems. The study, in general, found that there are two sources of pollutants from roofs. Materials deposited on the roof from wind and rain and compounds released through leaching mechanisms from the roofing material itself. It is clear that roofs negatively impact stormwater runoff quality because they are effective collectors of pollutants. These studies find that water collected from a roof should not be used as a potable water source without testing and treatment. This is due to pollutants such as bird faeces, bacteria, pesticides and herbicides carried by wind deposited on roofs. Small amounts of metals were found to leach from metal roofs or wood-treated shingles, as well as metal pollutants from flashing and gutters used to collect water. In the case of bituminous roofs, De Buyck states the following from his study: *"Furthermore, it should be noted that not all PAHs with 5 or more rings were systematically detected in the leachates, despite their presence in the bitumen matrix. Therefore, not all PAH species seem to be equally leached from the material. A higher log KOW and a lower solubility of these molecules might be the most important reasons for their absence in leachate. This is a prime example of the fact that total composition analysis is not suitable for assessing material leaching. (…) none of the consulted studies found a conclusive correlation between the bituminous material and the PAH concentrations in stormwater runoff"* [123].

Kriech et al. in 2022 published a review of the impact of stormwater and leaching from pavements on the environment. These included concrete, asphalt, and porous pavements since

1990. This study also found that stormwater pollutants can be a combination of atmospheric deposition and leaching. Additionally, pavements collect materials dropped from vehicles or spills on the pavement. Separating these from each other can be challenging, but based on the chemistry of the materials, they can generally be properly assigned to the source of the pollutants. The paper can be summarised as follows: *"Normally constructed asphalt and concrete pavements were found to release low levels of contaminants during their life. However, deposition from atmospheric pollutants and materials dispersed by vehicles on pavements do have a measurable impact on the quality of stormwater runoff. These tend to be expressed in initial flush from stormwater events. Porous pavements which allow water to pass through them are effective filters for removing particulates, organics, and metals. Materials such as water-soluble salts pass through them into groundwater. The challenge with porous pavements is that they tend to lose permeability over time from clogging of particulate and must be cleaned and maintained regularly"* (124).

The Kriech et al. study also found that pavement sealers containing coal tar pitch have high levels of polycyclic aromatic compounds and have been shown to impact aquatic life negatively and produce sediment buildup in ponds and streams, which must be handled in an environmentally responsible manner (124).

In 2020, Niles et al. reported on "Characterization of an Asphalt Binder and Photoproducts by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry Reveals Abundant Water-Soluble Hydrocarbons" (125). In this study, Niles placed films of bitumen on a glass slide and exposed the glass slide under water to simulate sunlight. The study found the process generated a significant amount of new water-soluble compounds.
In 2023, Crawford et al. conducted studies to better understand Niles' work (126). In the new study, the experiment was repeated and found to be consistent with Niles et al. However, the experiment, which was varied to better simulate pavements which are exposed to sunlight while dry followed by rainfall, produced minimal water-soluble compounds. This points out the importance of experimental design, which matches the uses of the materials to assess the environmental impact.

Glattke repeated the Niles experiment with pavement sealers in another study (127). This included bitumen-based as well as coal tar sealers. The study included Microtox testing of the water-soluble compounds generated in the Niles process. The study stated: *"The results demonstrate that coal tar sealant contains higher amounts of PAHs and produces abundant water-soluble compounds, relative to unweathered materials, with a high abundance of PAH-like molecules of high toxicity. By comparison, the asphalt sealant produces fewer toxic water-soluble species, with molecular compositions that are consistent with natural dissolved organic matter"* (127).

Bitumen pavements have a history of being recycled back into pavements since the 1970s. In 2021, Spreadbury conducted "A critical analysis of leaching and environmental risk assessment for reclaimed asphalt pavement management" (128). This study and the Kriech et al. 2022 review evaluated RAP for the environmental impact during removal, storage, and recycling or reuse, such as unbound granular bases under the pavement (124). Spreadbury found that the reviewed literature focuses on the leaching of metals and organic compounds; direct exposure risk was briefly reviewed and found not to exceed natural soils or aggregates. Kriech found that RAP was best stored on an impervious pad, and environmental pollutants that fall on or deposit on the pavement during its life can release low levels of PAHs and other pollutants in storage during rainfall events, especially during "first flush" rainfall events. Once these materials are re-used, they effectively remain within the new pavement.

8. SUSTAINABILITY

In 2015, the United Nations Member States identified and universally adopted 17 Sustainable Development Goals (SDGs) as a global blueprint to achieve a more prosperous and sustainable future for the planet and all its inhabitants. Four of the 17 SDGs fall within the immediate purview of the bitumen industry: "Industry, Innovation and Infrastructure," "Sustainable Cities & Communities," "Responsible Consumption & Production," and "Climate Action."

The "Paris Climate Agreement," also of 2015, focused the world's attention on the specific environmental sustainability goal of carbon neutrality. Members States of the European Union took a leading role in this effort by agreeing on the 2020 European Green Deal, which introduces a set of proposals to reduce carbon emissions to "Net Zero" by 2050 and decouple economic growth from resource use. Policies and regulations arising from the 2020 European Green Deal initiative will compel many businesses and industries, including the bitumen industry, to reduce their activities' potential environmental impacts, notably their carbon emissions.

Aligning with the 17 SDGs of the UN's 2015 global blueprint for a sustainable planet, with the objectives of the Paris Climate Agreement, and with the proposals of the European Green Deal, the United States Federal Highway Administration (FHWA) took a leadership role for the U.S. bitumen industry and laid out the following four guidelines to identify a sustainable pavement:

- Achieve the engineering goals for which they were constructed;
- Preserve and (ideally) restore surrounding ecosystems;
- Use financial, human, and environmental resources economically; and
- Meet human needs such as health, safety, equity, employment, comfort, and happiness.

These FHWA guidelines stipulate that to be considered "sustainable," pavements must meet the expected performance requirements. Along with this performance stipulation, these FHWA guidelines also require that "sustainable" pavements meet the triple-bottom-line sustainability principles of safeguarding the environment, using resources economically, and meeting all social needs satisfactorily. The same triple-bottom-line principles of sustainability apply to all the components in a bitumen pavement, including the key raw material, bitumen, and performance-enhancing additives and modifiers.

8.1 Sustainability requirements for the modern bitumen industry

The bitumen industry is a vital part of the construction sector of all healthy modern economies. To enhance the sustainability of the construction sector, many nations are modifying the policies and regulations regarding the environmental and social impacts of construction products. For example, the European Union introduced a new "Basic Works Requirement" (BWR) in the Construction

Products Regulation (CPR) of 2011 [129]. BWR 7 focuses on the "Sustainable Use of Natural Resources." Compliance with the BWR requires that product specifications incorporate environmental impact assessment criteria. Thus, under the auspices of the BWR, the European Commission has developed a series of criteria to assist member states in integrating green credentials into public procurement documents, including those relevant to road construction materials and installations. These procurement documents, which constitute Green Public Procurement criteria, are currently voluntary instruments. As such, they allow member states to decide which criteria and to what extent they are incorporated into a bidding process. However, as of 2023, several countries have already introduced requirements for information to be provided by bituminous materials suppliers. Other countries, including the USA, are modifying procurement policies to ensure economic, environmental, and social sustainability in bituminous pavements.

8.2 Opportunities for bituminous products and the construction sector today

Bitumen is a raw material used in paving and building construction products, including roofing applications. Therefore, the sustainability of bitumen cannot be considered separately from the life-cycle sustainability of the products it is used in. One significant advantage of bitumen is that it is never combusted post-production and provides serviceability through infrastructure. Bitumen is only heated during production because it is the non-distillate material contained within crude oil. Once in service, it never releases measurable levels of carbon dioxide into the atmosphere. Moreover, relative to other petroleum products, bitumen has an extremely long life cycle and can be re-used at the end of the service life of the construction.

At the end of its life cycle, an aged bitumen pavement can be reclaimed and recycled into many valuable products within the pavement construction industry. RAP has been used routinely in pavement construction since the 1970s. Many pavements have been recycled multiple times over the past 50 years without detriment to the pavement performance. Despite the apparent advantages of bitumen, policy requirements mandate scientific substantiation of its sustainability benefits.

So, although the sustainability of bituminous products such as bitumen pavements has been demonstrated for decades, conformance with today's administrative policies and regulatory guidelines, such as those in the European Union's Basic Work Requirement, means that bitumen industry stakeholders must substantiate the sustainability benefits of their products according to uniform scientific procedures in compliance with rules established by the International Standards Organization (ISO).

To address the environmental sustainability of bituminous products, both the Asphalt Institute (AI) and Eurobitume have conducted ISO-compliant cradle-to-gate life cycle assessment (LCA) studies for the respective geographic markets. A key impact factor identified through AI and Eurobitume's LCA studies is crude oil extraction and transportation. The results of both LCA studies showed that the bitumen refining and storage stages typically constituted to less than 20% of the cradle-to-gate impact (depending upon the impact category).

Polymers/modifiers are also added to bitumen to enhance material durability and, subsequently, the lifetime of a pavement/roof and, therefore, reduce the product's environmental impact over the whole life-cycle period. Third-party research (Asphalt Institute Informational Series 215 – Quantifying the Effects of PMA for Reducing Pavement Distress) shows that polymer-modified bitumen roads increased durability and service life compared to unmodified bitumen roads (130). This is expected to reduce life cycle carbon emissions by reducing rehabilitation cycles, less traffic interruption, increased construction worker and public safety, and reduced energy consumption. Other modifiers and additives are crucially important to bitumen pavement durability. Warm mix additives and adhesion promoters are notable in this regard.

Bitumen as a source material for binders offers the capability of being fully recyclable and reused in various industry applications, including paving and roofing. From the 2021 Usage Survey of the National Asphalt Pavement Association: The bitumen industry remains the country's most diligent recycler, with more than 99% of reclaimed asphalt pavement being put back to use. Respective data are available from individual European countries via EAPA (131) (132).

Recyclability is an important criterion of bitumen pavement sustainability. The Asphalt Institute and Eurobitume are open to proven new technologies involving recycling techniques and/or the use of secondary materials. However, all initiatives to increase recycling should be based on sound science and quantify the net benefits to society across the entire lifecycle. For example, as per the Recycled Materials policy published by the FHWA in 2015, any material used in highway or bridge construction, be it virgin or recycled, shall not adversely affect the performance, safety, or the environment of the highway system.

Hence, the following key topics should be considered when using recycled, secondary, or waste streams in bitumen from a sustainability perspective:

- The holistic sustainability covering the performance, cost, environmental and social aspects of systems such as pavements, roofs and others containing bitumen products should not be negatively impacted by the addition of secondary materials, additives, or waste streams.

All sustainability decisions should be based on credible, robust research and development work by experts in the related field.

APPENDIX 1

List of Abbreviations and Glossary

Abbreviations

%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's gravity is approximately 9.8m.s-$^{1)}$

mg SI notation for milligram

µg SI notation for microgram

m^3 SI notation for cubic metre

AASHTO American Association of State Highway and Transportation Officials

ACGIH American Conference of Governmental Industrial Hygienists

ASTM, ASTM INTERNATIONAL Formerly known as American Society of Testing and Materials, as of 2001 name changed to ASTM International. An organisation that develops and delivers voluntary consensus standards.

CAS# Chemical Abstract Services Registry Number

CEN Comité Europeen de Normalisation

CLP Classification Labeling and Packaging

CONCAWE CONCAWE is an organisation of European Oil Companies for Environment, Health and Safety. The acronym stands for CONservation of Clean Air and Water in Europe.

DHHS Department of Health & Human Services (A US Government agency)

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.

EVT Equi-Viscous Temperature

GC/MS Gas Chromatography-Mass Spectrometry

GHS Globally Harmonised System

NIOSH National Institute of Occupational Safety and Health

OEL Occupational Exposure Limit

OSHA Occupational Safety and Health Administration

PAH/PAC Polycyclic Aromatic Hydrocarbon, Polycyclic Aromatic Compounds

PMB/PMA Polymer-Modified Bitumen/Asphalt

PNA PolyNuclear Aromatic

PPA Polyphosphoric Acid

PPE Personal Protective Equipment

PPM Parts Per Million

RAP Reclaimed Asphalt Pavement

RAS Reclaimed Asphalt Shingles

REACH Registration, Evaluation Authorisation of Chemicals (European Chemicals regulation EC No 1907/2006

REOB Re-refined Engine Oil Bottoms

REL Recommended Exposure Limit

RLOB Re-refined Lube-Oil Bottoms

TLV Threshold Limit Value

TSCA Toxic Substances Control Act

VTAE Vacuum Tower Asphalt Extender

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 they are common expressions used in the bitumen supply chain.

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 BITUMEN**.

AIR-BLOWN ASPHALTS
See **OXIDISED BITUMEN**.

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

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 bitumen is functionally the same as straight-run bitumen. Air-rectified bitumen is used in paving applications as well as selected roofing applications, such as shingle saturants and Type 1 Built Up Roofing Asphalt (BURA), and also for some industrial applications. AIR-RECTIFIED BITUMEN have a **PENETRATION INDEX** (PI) ≤+2.0.

API GRAVITY - API gravity is a commonly used index of the density of a crude oil or refined products. API stands for the American Petroleum Institute, which is the industry organization that created this measure.

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**. The use of the term **ASPHALT CEMENT** is decreasing in favor of **ASPHALT BINDER**. Historically **ASPHALT CEMENT** referred to bitumen products that contained no modifiers or additives.

ASPHALT COLD MIXES
ASPHALT mixtures are made using **CUT-BACK BITUMEN** 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 **BITUMEN**. They can be precipitated with n-heptane and are sometimes referred to as n-heptane insolubles.

ASPHALT MASTIC
A term of art in asphalt mixture technology referring to the combination of bitumen and the fine mineral portion of the aggregate generally comprised of mineral matter finer than 150 µm.

ASPHALT MIXES (MIXTURES)
Mixtures of graded mineral aggregates (sized stone fractions, sands and fillers) with a controlled amount of **BITUMEN**.

ATMOSPHERIC DISTILLATION
Distillation at atmospheric pressure.

ATMOSPHERIC RESIDUUM
Residuum of **ATMOSPHERIC DISTILLATION** of **CRUDE OIL**.

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 **BITUMEN** to resist low temperature cracking of pavements.

BENDING BEAM RHEOMETER (BBR)
A machine used to determine the low temperature stiffness properties of BITUMEN 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 EN 12597; 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 utilise **MODIFIED BITUMEN**.

BINDER REPLACEMENT RATIO, BINDER REPLACEMENT %
When **RECLAIMED ASPHALT PAVEMENT** (RAP) or **RECLAIMED ASPHALT SHINGLE** (RAS) is added to a bituminous paving mixture the ratio of the amount of bitumen contributed by the **RAP/RAS** to the total bitumen content of bituminous paving mixture is referred to as the **BINDER REPLACEMENT RATIO**. Older terminology referred to the ratio as a percent and therefore **BINDER REPLACEMENT** % can still be found in the literature.

BIO-BINDERS / BIO BITUMEN, BIO-FLUXED BITUMEN
A general term applied to a variety of petroleum bitumen alternatives produced solely from non-petroleum, renewable chemical sources or from blends of non-petroleum, renewable chemical sources and conventional petroleum bitumen. These non-petroleum sources include but are not limited to vegetable oils (generally reacted to substantially remove fatty acid functionality), tall oil fatty acid derivatives, tall oil rosin acid derivatives, lignin, cashew nut shell oil (urushiol), vegetable-based waxes, and many others.

BIO REJUVENATORS
Term applied to non-petroleum-derived, renewable and generally vegetable or tall-oil based softening agents added to petroleum-based bitumen to improve the performance of the blended product with **RAP** and/or **RAS** containing asphalt mixtures.

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 residuums of different stiffness characteristics.

BITUMEN EMISSIONS
The complex mixture of aerosols, vapours and gases from heated **BITUMEN** and products containing bitumen; although the term "**BITUMEN FUME**" is often used in reference to total emissions, technically bitumen fume does not include gases (i.e. solid particulate matter, aerosols and vapour).

BITUMEN EMISSION (FUME) CONDENSATE see also ASPHALT FUME CONDENSATE
The condensate of emissions from heated BITUMEN; the chemical composition may vary with the temperature and type of bitumen. It typically has a boiling range similar to kerosene.

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

BITUMEN EXTRACT
The fraction of **BITUMEN** that is soluble in organic solvents, such as benzene, toluene, carbon disulphide, or dimethyl sulphoxide.

BITUMEN FUME
The complex mixture of vapors and aerosols emitted from heated **BITUMEN**.

BITUMEN GRADING TERMINOLOGY
There are currently three main grading systems employed world-wide for identifying and specifying **BITUMEN** 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 **BITUMEN** is 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 **CUT-BACK BITUMEN** 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 specialised **CUT-BACK BITUMEN** product that contains relatively small amounts of other materials that are not native to **BITUMEN** or to the diluents typically used in cut-back products, such as lamp-black, aluminium flakes, and mineral pigments. They are used as a protective coating in waterproofing operations and other similar applications.

BITUMEN PRIMER
A CUT-BACK BITUMEN made to treat bare metal surfaces giving a bond between the metal and an **ENAMEL**. In North America, a **PRIMER** is a spray coating to bond an underlying layer to the first layer of **HOT MIX ASPHALT**. As such, it can be a **BITUMEN CUT-BACK** or **BITUMEN EMULSION**.

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

BITUMEN VAPOUR
Refers to vapours which can include gases from heated **BITUMEN**.

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

BLENDED BITUMEN
Blends of two or more grades of **BITUMEN** with different physical characteristics or blends of **BITUMEN**.

BLOWING STILL
(Also known as **OXIDISER**, Bitumen Blowing Unit, or Bitumen Oxidation Unit.) Equipment used to oxidise **BITUMEN**.

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

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 fibre) 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 fibre) 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.

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

CAS REGISTRY NUMBER
A number is assigned to a substance when it enters the **CAS REGISTRY** database.

CATALYTIC AIR-BLOWN BITUMEN
OXIDISED BITUMEN 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** and/or **POLYMER MODIFIED BITUMEN** used to manufacture roofing membranes or shingles.

COLD ADHESIVE
Bituminous **CUT-BACK** 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 workplace without any heating (e.g. peel and stick bitumen membrane or membranes applied with the use of a cold adhesive).

COLD IN-PLACE RECYCLING (CIR)
Utilisation of an integrated system to grind or mill existing bituminous pavement to a size generally smaller than 37.5mm and incorporate new **BITUMEN** with an integrated mixing system into the reclaimed material followed by spreading or using an integrated paving machine to produce a road surface which is then compacted to a target density. The new **BITUMEN** is in the form of a **BITUMEN EMULSION** or a foamed bitumen.

COLLOID MILL
High-speed shearing device 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 coloured minerals used as light surface protection for **BITUMEN** membranes or bitumen shingles.

CRACKING-RESIDUE BITUMEN [THERMAL BITUMEN]
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.

CUT-BACK BITUMEN (PETROLEUM)
BITUMEN whose viscosity has been reduced by the addition of a **CUT-BACK SOLVENT** derived from petroleum.

CUT-BACK SOLVENT (PETROLEUM)
Relatively volatile petroleum solvent used in the manufacture of **CUT-BACK 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 a significant proportion of the dispersion medium for the **ASPHALTENES** and adsorbed resins in **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 **BITUMEN** over a range of temperatures and test frequencies. Typically, a standard amount of **BITUMEN** (25mm diameter by 1mm thickness) tested between two flat plates (25mm 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**.

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 vulcanised 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 between aggregate particles.

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.

FLASH POINT
The temperature at which a combustible vapour 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 Flash point and EN ISO 2719 or ASTM D93 for Closed Cup Flash point.

FLEXIBLE PAVEMENTS
Road surfacings made from layers of **ASPHALT** mixtures.

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 **CUT-BACK BITUMEN** which also are reduced viscosity **BITUMEN** in that the flux oils have negligible volatility at ambient temperatures compared to the petroleum solvents used to produce **CUT-BACK BITUMEN**.

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 straight-run bitumen from which **OXIDISED BITUMEN** is made. Typically soft **BITUMEN** [less than 50 Pa·s@60°C (140°F)] are used, although **BITUMEN** of higher viscosity can be included within the definition of FLUX.

Europe: Fluxes are also used in the manufacture of oxidised bitumen in the EU.

FLUX OILS (PETROLEUM)
Relatively non-volatile 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 BITUMEN
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 **BITUMEN**.

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 northeastern Utah, USA.

GLASS MAT OR FELT
A non-woven mat made with short glass fibres adhered together with a resin and suitable for coating and impregnation with **BITUMEN** for roofing products.

GROUND TIRE RUBBER (GTR) MODIFIED BITUMEN
BITUMEN to which rubber reclaimed from scrap tyres and ground to various mesh sizes has been added. The tyre rubber mesh size various depending on the specific processing method being employed. Mesh size used can be as large as 20 mesh (0.841mm) and as small as GTR finer than 80 mesh (0.177mm).

HARD BITUMEN
A rheologically stiff 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**.

HEAT WELDED 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
Site workers that perform miscellaneous tasks on work sites.

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, also part of EN 12607-1 & -2.

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.

MILLING or MILLING MACHINE
Milling is the term applied to the use of machine comprising a large rotating mandrel with carbide steel teeth attached to the surface of the mandrel capable removing existing **ASPHALT** from the road surface. This milled **ASPHALT** is fed on an integrated conveyer to trucks which haul the milled **ASPHALT** to a central location where it is stockpiled and ultimately incorporated as **RAP** into a new **ASPHALT** pavement.

MINERAL AGGREGATE
A combination of stone fractions and **FILLER**.

MODIFIED BITUMEN
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.

THE MULTIPLE STRESS CREEP RECOVERY (MSCR) PROCEDURE
A rheological test performed on a **DYNAMIC SHEAR RHEOMETER (DSR)** to determine the non-recoverable compliance of a **BITUMEN**. **NON-RECOVERED COMPLIANCE of a BITUMEN** has been shown to correlate to the **BITUMEN'S** contribution to the rutting resistance of an **ASPHALT MIXTURE.**

NATURAL ASPHALT
Naturally-occurring mixture of **BITUMEN** and mineral matter formed by oil seepages in the earth's crust then evaporating through geological forces. Natural asphalts include Trinidad Lake, Rock, Gilsonite, Selenice and others.

NON-RECOVERED COMPLIANCE
A measure of the resistance to permanent deformation that a bitumen in an asphalt mixture contributes to the pavement. Low values of non-recovered compliance, for example values less than 1 kPa^{-1} or less than 0.5 kPa^{-1}, at a given pavement temperature are very resistant to permanent deformation under heavy or extreme loading conditions.

OIL (PETROLEUM) VACUUM DISTILLATION BOTTOMS, USED [CAS# 129893-17-0]
A very complex combination of high molecular weight hydrocarbon consisting mostly of spent polymers and organometallic based additives which have been removed as a non-volatile residue from waste lubricating oils. This material consists primarily of hydrocarbons with a carbon number greater than 25, and with high carbon to hydrogen ratios. This material will contain metals such as zinc, calcium, sodium and magnesium. Numerous trade names exist for this material including **RE-REFINED ENGINE OIL BOTTOMS and, VACUUM TOWER ASPHALT EXTENDER.**

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 fibre 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 (PAH) 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). PAC can include atoms other than carbon and hydrogen, such as nitrogen, oxygen or sulphur.

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 BITUMEN

BITUMEN classified by the depth to which a standard needle will penetrate the **BITUMEN** sample under specified test conditions (see ASTM D5 and/or EN 1426 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**.
A **PENETRATION INDEX** of zero is attributed to a bitumen with a **PENETRATION** at 25°C (77°F) of 200 x 0,1mm and a **SOFTENING POINT** of 40°C (104°F).
The **PENETRATION INDEX** is calculated as follows (according to EN 12591);

$$I_p = \frac{20 \times t_{RaB} + 500 \times \lg P - 1952}{t_{RaB} - 50 \times \lg P + 120}$$

PENETRATION TEST

Specification test to measure the hardness of **BITUMEN** under specified conditions. In which the indentation into a **BITUMEN** in tenths of a millimeter (0,1mm) at 25°C (77°F) is measured using a standard needle with a loading of 100g and 5s duration. Details of the test can be found in ASTM D5 and/or EN 1426 as well as other sources.

PERFORMANCE GRADED BINDERS

BITUMEN 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 BITUMEN** are most widely utilised in the United States and Canada and conform to specifications as stipulated in ASTM D6373, AASHTO M320 and AASHTO M332.

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 – 180°C (104 – 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 **BITUMEN** 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: $H^6P^4O^{13}$.
POLYPHOSPHORIC ACID includes long-chain polymerised units of PO4 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**.

RAP
Acronym for Reclaimed or Recycled Asphalt Pavement. In practice existing asphalt pavement is removed from the roadway and crushed to a useable dimensions (generally less than 25mm) and incorporated at some percentage into a new paving material. Typically, **RAP** has been added to bituminous paving mixtures in amounts equivalent to **BINDER REPLACEMENT RATIOS** of 0.10 to 0.25. Recently research has sought to find methods to increase this ratio to as much as 0.50.

RAS
Acronym for Reclaimed Asphalt Shingles. In practice post-consumer waste shingles are ground to a size generally smaller than 12.5mm which is then incorporated in bituminous paving mixtures. Typically 3% to 6% RAS is added to a bituminous mixture resulting in a **BINDER REPLACEMENT RATIO** of approximately 0.15 to 0.25.

RE-REFINED ENGINE OIL BOTTOMS (REOB)
See **OIL (PETROLEUM) VACUUM DISTILLATION BOTTOMS, USED**.

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

REJUVENATOR
Term applied to any type of **FLUXING OIL** or softening agent added to a **BITUMEN** with the express intent of altering the rheological and compositional properties of aged **BITUMEN** that is incorporated into the **ASPHALT MIXTURE**. The aged Bitumen added to the asphalt mixture is generally incorporated through the addition of **RAP** and/or **RAS** materials. There is currently no consensus among bitumen technologists as to whether true rejuvenation of aged **BITUMEN** occurs or whether all such rejuvenators only function to soften the **BITUMEN** to which they are added and therefore reduce the overall stiffness of the total asphalt mixture.

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 RESIDUUM** or harder **BITUMEN** that have **FLUX OIL** added, or **CUT-BACKS** 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, USA 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 75-85 minutes. See ASTM D2872, or EN 12607-1. The test was designed to simulate aging of the Bitumen through the Hot-Mix plant.

ROOFER'S FLUX (also called **ROOFING FLUX**)
A low viscosity, high flash point, 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 **CUT-BACK 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, SATURATED 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 coloured 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 **BITUMEN**, together with alkyl naphthenes and some alkyl aromatics. This fraction forms 5–20% of the mass of **BITUMEN**.

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
Synonym for AIR-RECTIFIED BITUMEN.

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 ºC, at which material under standardised test conditions attains a specific consistency (see ASTM D36 and/or EN 1427).

SOLVENT EXTRACTS
Aromatic by-products (extracts) obtained from the refining of **BASE OILS**.

SOLVENT PRECIPITATION
The process by which a hard product, **PROPANE-PRECIPITATED ASPHALT**, is separated from a **VACUUM RESIDUUM** by solvent precipitation (usually with propane). In the USA, this process is called 'solvent deasphalting' and the product, **SOLVENT-REFINED ASPHALT**.

SOLVENT-REFINED ASPHALT
Term used in the USA for **PROPANE-PRECIPITATED ASPHALT**, also referred to PDA pitch or PDA asphalt.

SPECIFIC GRAVITY
A dimensionless parameter relating the density of a material to that of a specifc reference material. The reference material is usually water.

STEAM-REFINED BITUMEN
VACUUM RESIDUUMS that have been subjected to **STEAM-STRIPPING**. Archaic term.

STEAM STRIPPING
Injection of steam into a residuum 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 **ASPHALT** mixtures.

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

STRAIGHT-REDUCED BITUMEN
Similar to **STRAIGHT-RUN BITUMEN** and **STEAM-REFINED BITUMEN**.

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

SULPHUR EXTENDED ASPHALT
A hot mixed **ASPHALT** in which part of the **BITUMINOUS BINDER** is replaced by elemental sulphur, typically at levels between 20–40%m of the original bitumen content.

SURFACE DRESSING (Synonym for CHIP SEAL)
Process used to seal road surfaces; a thin film of bitumen, **CUT-BACK 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 waterproof a surface. It is normally covered with aggregate to provide friction to the roadway.

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.

TERMINAL BLENDED CRUMB RUBBER MODIFIED BITUMEN
Generally consists of blending ground tire rubber of a size range from 600μm to 177μm (30 to 80 mesh) with asphalt binder at temperatures ranging from 175 to 190°C (≈ 350 to 375°F) and allowing them to react for 60 (+) minutes prior to transfer to large storage tanks. Once mixed, the rubber modified asphalt is stored at elevated temperatures.

THERMALLY CRACKED BITUMEN
Also known as Residues (petroleum), thermal cracked, vacuum: **BITUMEN** produced by thermal cracking, followed by vacuum distillation.

THERMOPLASTIC POLYMER (PLASTOMER)
A polymer type which exhibits stiffness and strength but does not recover substantially when deformed. Examples of this type of polymer used in **BITUMEN** are ethylene vinyl acetate, ethylene methacrylate, polyethylene, and atactic polypropylene.

TOPPING PLANT
A 'stand-alone' distillation plant. Topping plants are usually found in terminals and used to remove distillate materials added to **BITUMEN** 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 RESIDUUM** under vacuum.

VACUUM TOWER ASPHALT EXTENDER
Terminology endorsed by the National Oil Recyclers Association applied to Used Oil Vacuum Tower Distillation Bottoms and described by CAS# 128983-17-0. These materials have been added to **BITUMEN** to change the low temperature properties and to enhance the oxidation of some bitumen roofing products. Numerous other terms have been employed by the producers and users of this type of additive. When used in paving the material is added up to 10% to soften the **BITUMEN** for use with RAP or RAS or meet cold weather requirements. When used in **OXIDISED ASPHALT** it is added up to 6% as a paraffinic oil to increase penetration.

VACUUM RESIDUUM
Residue obtained by **VACUUM DISTILLATION**.

VISBREAKING
A relatively mild thermal cracking operation mainly used to reduce the viscosity and pour point of **VACUUM RESIDUUMS** for subsequent use in heavy fuel oils. The process converts a proportion of the residuum 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 utilise **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 or dense graded **HOT MIX ASPHALT** pavement. **WARM-MIX ASPHALTS** are produced and placed at temperatures typically 10 – 40°C (50 – 100°F) lower than conventional rolled or dense graded **ASPHALT**.

WEATHERING TEST
Various accelerated durability tests have been developed for **OXIDISED BITUMEN** used in roofing applications. The most prevalent is the Xenon Arc Accelerated Weathering test, where thin **OXIDISED BITUMEN** films are applied to aluminium 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 bitumen

European and US Inventory Status: Commonly used bitumen streams

		Regulatory Entities			
CAS Registry #		**EINECS #**	**REACH***	**TSCA**	**DSL/ NDSL**
8052-42-4	**Asphalt** 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.	232-490-9	R	Listed	DSL
64741-56-6	**Residues (petroleum), vacuum** A complex residuum from the vacuum distillation of the residuum from atmospheric distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly greater than C34 and boiling above approximately 495oC (923oF).	265-057-8	R	Listed	DSL
64742-85-4	**Residues (petroleum), hydrodesulfurized vacuum** 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 495oC (923oF).	265-188-0	R	Listed	DSL
64742-93-4	**Asphalt, oxidized** 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.	265-196-4	R	Listed	DSL

		Regulatory Entities			
CAS Registry #		**EINECS #**	**REACH***	**TSCA**	**DSL/ NDSL**
91995-23-2	**Asphaltenes (petroleum)** A complex combination of hydrocarbons obtained as a complex solid black product by the separation of petroleum residues by means of a special treatment of a light hydrocarbon cut. The carbon/hydrogen ratio is especially high. This product contains a low quantity of vanadium and nickel.	295-284-8	PR	Not Listed	Not Listed
92062-05-0	**Residues (petroleum), thermal cracked vacuum** A complex combination of hydrocarbons obtained from the vacuum distillation of the products from a thermal cracking process. It consists predominantly of hydrocarbons having carbon numbers predominantly greater than C34 and boiling above approximately 495oC (923oF).	295-518-9	R	Not Listed	Not Listed
94114-22-4	**Residues (petroleum), dewaxed heavy paraffinic, vacuum** A complex combination of hydrocarbons obtained as the residue from the molecular distillation of a dewaxed heavy paraffinic distillate. It consists of hydrocarbons having carbon numbers predominantly greater than C80 and boiling above approximately 450oC (842oF).	302-656-6	PR	Not Listed	Not Listed
100684-39-7	**Residues (petroleum), distn. residue hydrogenation** A complex combination of hydrocarbons obtained as a residue from the distillation of crude oil under vacuum. It consists predominantly of hydrocarbons having carbon numbers predominantly in the range above C50 and boiling in the range above approximately 360oC (680oF).	309-712-9	PR	Not Listed	Not Listed
100684-40-0	**Residues (petroleum), vacuum distn. residue hydrogenation** A complex combination of hydrocarbons obtained as a residue from the distillation of crude oil under vacuum. It consists predominantly of hydrocarbons having carbon numbers predominantly in the range above C50 and boiling in the range above approximately 500oC (932oF).	309-713-4	PR	Not Listed	Not Listed
64742-16-1	**Petroleum Resins** 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.	N/A	NR	Listed	DSL
64742-07-0	**Raffinates (petroleum), residual oil decarbonization** 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 495oC (923oF).	N/A	NR	Listed	DSL

*R=Registered
PR=Preregistered
NR=No Registration for bitumen use

Health Classifications of Bitumen by Various Agencies and Authorities

Agency	Substance	Classification
American Conference of Governmental Industrial Hygienists	Asphalt (bitumen) fumes [8052-42-4]	A4 - Not Classifiable as a Human Carcinogen
International Agency for Research on Cancer (2013)	Occupational exposures to hard bitumen and their emissions during mastic-asphalt work Occupational exposures to oxidized bitumen and their emissions during roofing [64742-93-4] Occupational exposures to straight-run bitumen and their emissions during road paving [8052-42-4, 64741-56-6]	Group 2B – Possibly Carcinogenic to Humans Group 2A – Probably Carcinogenic to Humans Group 2B – Possibly Carcinogenic to Humans
California Safe Drinking Water and Toxic Enforcement Act	Extracts of steam-refined and air-refined bitumen	Listed as carcinogen
European Union Classification (Annex VI of CLP-Regulation (EC) No 1272/2008	Bitumen Asphalt, Oxidized	Not classified Not classified
US National Institute for Occupational Safety and Health	Asphalt Fumes	NIOSH Carcinogen List
US National Toxicology Program	Asphalt Fumes	Evaluation deferred
CONCAWE (The Oil Companies' European Association for Environment, Health and Safety in Refining and Distribution): Report No. 8/12, 2012	Bitumen Asphalt, Oxidized	Not classified Not classified

APPENDIX 3

Occupational Exposure Limits for Bitumen Emissions

Note: This table is believed to be accurate as of the date of publication (2024). Occupational Exposure Limits are updated periodically and the information should be checked regularly for updates.

https://ilv.ifa.dguv.de/limitvalues/3923

APPENDIX 4

Properties and Specifications

Properties

Property in IS-230	Name	Standard US	Standard EN
Penetration	Needle penetration	AASHTO T-49, ASTM D-5	EN 1426
Softening Point	Softening Point Ring and Ball	AASHTO T-53, ASTM D-36	EN 1427
Penetration Index	Penetration Index PI		EN 12591
Pour point		ASTM D-9895	
Breaking point	Fraass Breaking Point		EN 12593
Plasticity range	Difference between Softening Point Ring and Ball and Fraass Breaking Point		EN 12591
Dynamic Shear Rheometer	Complex Shear Modulus G* and phase angle	ASTM D-7175	EN 14770

Specifications

Europe

EN 12591:2009 - Bitumen and bituminous binders - Specifications for paving grade bitumen

EN 13304:2009 - Bitumen and bituminous binders - Framework for specification of oxidised bitumen

EN 13305:2009 - Bitumen and bituminous binders - Framework for specification of hard industrial bitumen

EN 13808:2013 - Bitumen and bituminous binders - Framework for specifying cationic bituminous emulsions

EN 13924-1:2016 - Bitumen and bituminous binders - Specification framework for special paving grade bitumen - Part 1: Hard paving grade bitumen

EN 13924-2:2014 - Bitumen and bituminous binders - Specification framework for special paving grade bitumen - Part 2: Multigrade paving grade bitumen

EN 14023:2013 - Bitumen and bituminous binders - Specification framework for polymer modified bitumen

EN 15322:2013 - Bitumen and bituminous binders - Framework for specifying cut-back and fluxed bituminous binders

U.S.

AASHTO M 320-23 - Standard Specification for Performance-Graded Asphalt Binder

AASHTO M 332-23 - Standard Specification for Performance-Graded Asphalt Binder Using Multiple Stress Creep Recovery (MSCR) Test

AASHTO M 140-20 - Standard Specification for Emulsified Asphalt

AASHTO M 208-20 - Standard Specification for Cationic Emulsified Asphalt

AASHTO M 316-23 - Standard Specification for Polymer-Modified Emulsified Asphalt

AASHTO M 81-92 (2021) - Standard Specification for Cut-back Asphalt (Rapid-Curing Type)

AASHTO M 82-17 (2021) - Standard Specification for Cut-back Asphalt (Medium-Curing Type)

International

ASTM D6373-23 - Standard Specification for Performance-Graded Asphalt Binder

ASTM D8239-23 - Standard Specification for Performance-Graded Asphalt Binder Using the Multiple Stress Creep and Recovery (MSCR) Test

ASTM D977-20 - Standard Specification for Emulsified Asphalt

ASTM D2397-20 - Standard Specification for Cationic Emulsified Asphalt

ASTM D2026-15 (2021) - Standard Specification for Cut-back Asphalt (Slow-Curing Type)

ASTM D2027-19 - Standard Specification for Cut-back Asphalt (Medium-Curing Type)

ASTM D2028-15 (2021) - Standard Specification for Cut-back Asphalt (Rapid-Curing Type)

ASTM D312-16a (2023) - Standard Specification for Asphalt Used in Roofing

ASTM D449-03 (2021) - Standard Specification for Asphalt Used in Dampproofing and Waterproofing

ASTM D2521-76 (2021) - Standard Specification for Asphalt Used in Canal, Ditch, and Pond Lining

ASTM D3141-21 - Standard Specification for Asphalt for Undersealing Portland-Cement Concrete Pavements

APPENDIX 5

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; *Am J Ind Med*, Vol 43, 1, 2003.

World Health Organisation "Concise International Chemical Assessment Document 59" 2005, available at http://www.who.int/ipcs/publications/cicad/cicad59_rev_1.pdf

Proceedings of "The Health Effects of Occupational Exposure to Emissions from Asphalt/Bitumen Symposium", June 7-8, 2006, Dresden, Germany; *J Occup Environ Hyg*. Vol 4, Supplement 1, 2007.

A case-control study of lung cancer nested in a cohort of European asphalt workers. *Environ Health Perspect*. 2010 Oct; 118(10):1418-24.Epub 2010 Jun 9.

IARC Monograph Volume 103 on "Bitumen and Bitumen Emissions and some N- and S-Heterocyclic Polycyclic Aromatic Hydrocarbons" 2013, available at http://monographs.iarc.fr/ENG/Monographs/vol103/index.phpAll Robbins Office Park <AllRobbinsOfficePark@asphalt-materials.com>

APPENDIX 6

Summary of Refinery Sector Exposure Data

Occupation	Source of exposure	Number	Type	Range (mg/m³)	Geo. Mean	Ari. mean	Ref	Source
General asphalt refinery workers	Vacuum distillation	4*	Total PAHs†	0.0047-0.016	0.0082	0.0095	NIOSH 1980[1]	NIOSH Hazard Review
General asphalt refinery workers	Asphalt processing (6 refineries)	14*	Total PAHs†	0.0015-0.031	0.067	0.010	NIOSH 1983[2]	NIOSH Hazard Review
General asphalt refinery workers	Deasphalting (1 refinery)	4*	Total PAHs†	0.0014-0.041	0.12	0.021		NIOSH Hazard Review
Assistant operator		3	Total PAHs†	0.0025-0.050	0.14	0.025		NIOSH Hazard Review
Bitumen loaders	Outdoor bitumen refinery unit (bitumen at 170 to 210°C [338 to 410°F])	‡	Benzene solubles	0.3-1.0	§	§	Claydon et al.1984[3]	NIOSH Hazard Review
		‡	Total particulates	0.1-1.4	§	§		NIOSH Hazard Review
Package fillers	Indoor area (bitumen at 220°C [428°F])	2	Total particulates	0.20-0.32	0.25	0.23	Brandt et al.1985[4]	NIOSH Hazard Review
Bitumen loaders	Outdoor bitumen refinery unit (bitumen at 170 to 210°C [338 to 410°F])	4	Total particulates	0.7-2.9	§	1.4		NIOSH Hazard Review
Operator		11	Total particulates	<0.03-8.2	0.17	0.88	Hicks 1995[5]	NIOSH Hazard Review
		11	Benzene solubles	0.034-1.9	0.14	0.42		NIOSH Hazard Review

Occupation	Source of exposure	Number	Type	Range (mg/m^3)	Geo. Mean	Ari. mean	Ref	Source
Assistant operator	Asphalt refinery/ terminal (temperature of product at fume source ranged from 160 to 375°C [320 to 707°F])	9	Total particulates	<0.03-0.49	0.18	0.25	Hicks 1995[5]	NIOSH Hazard Review
		9	Benzene solubles	<0.066-0.32	0.11	0.13		NIOSH Hazard Review
		4	Total particulates	0.17-0.26	0.22	0.23		NIOSH Hazard Review
Lab technician		4	Benzene solubles	<0.062-0.43	0.15	0.21		NIOSH Hazard Review
Loader/Pumper operator		10	Total particulates	<0.026-14	0.29	1.6		NIOSH Hazard Review
		10	Benzene solubles	0.038-13	0.29	1.6		NIOSH Hazard Review
Maintenance/ Administration	Asphalt refinery/ terminal (temperature of product at fume source ranged from 160 to 375°C [320 to 707°F])	6	Total particulates	<0.032-0.77	0.17	0.29		NIOSH Hazard Review
		6	Benzene solubles	0.011-0.22	0.076	0.1		NIOSH Hazard Review
Utility worker		4	Total particulates	<0.024-0.062	0.039	0.043		NIOSH Hazard Review
		4	Benzene solubles	<0.054-1.1	0.3	0.49		NIOSH Hazard Review
General refinery workers			Hydroxypyrene				Boogaard et al 1995[6]	
Refinery road tanker loading	Various Pen and Oxidised Grades (170-210°C [338-410°F])]	4	Total particulates	0.7-2.9			Brandt et al[4]	
General refinery Workers	Vacuum distillation		Total PACs	1.8-19$µg/m^3$			Futagaki et al 1981[7]	IARC mon #35 (same ref as NIOSH 1983)

Occupation	Source of exposure	Number	Type	Range (mg/m^3)	Geo. Mean	Ari. mean	Ref	Source
Office worker	Bitumen Terminal	6	TPM BSM	0.04-0.29 0.03-0.08	0.08 0.04	0.12 0.04	Gamble[8]	
Lab technician	Bitumen Terminal	7	TPM BSM	0.08-0.64 0.03-0.11	0.23 0.05	0.3 0.06		
Loader	Bitumen Terminal	14	TPM BSM	0.07-0.58 0.03-0.11	0.2 0.04	0.23 0.04		
Manager	Bitumen Terminal	4	TPM BSM	0.08-0.77 0.03-0.09	0.26 0.05	0.35 0.05		
Misc.	Bitumen Terminal	10	TPM BSM	0.03-2.51 0.03-0.2	0.19 0.09	0.43 0.2		
Loader/Pumper	Refinery/Terminal	10	TPM BSM	<0.026-14 0.038-13	0.29 0.29	1.6 1.6	Hicks[5]	Further information to be found in full citation
Operator	Refinery/terminal	11	TPM BSM	<0.03-8.2 0.034-1.9	0.17 0.14	0.88 0.42		
Driver/Loader	Truck loading gantry	3	TPM (UK HSE MDHS#70)	<0.01 – 0.3 mg/m^3 8hr TWA	NA	NA	Company Report	Unpublished UK production facility 1999
Plant operator	Bitumen unit during shutdown duties	1	TPM (UK HSE MDHS#70	0.1 mg/m^3 8hr TWA	NA	NA	Company Report	Unpublished UK production facility 1999
Driver/Loader	Truck loading gantry	6	TPM (UK HSE MDHS#14/2)	0.6 – 3.0 (mg/m^3 15 min STEL)	NA	NA	Company Report	Unpublished UK production facility 2001
Driver/Loader	Truck loading gantry (100/150pen)	1	TPM (UK HSE MDHS#14/2)	0.66 (mg/m^3 15 min STEL)	NA	NA	Company Report	Unpublished UK production facility 2002
Driver/Loader	Truck loading gantry (40/60pen)	1	TPM (UK HSE MDHS#14/2)	4.33 (mg/m^3 15 min STEL)	NA	NA	Company Report	Unpublished UK production facility 2002
Aid'operateur	Bitumen truck loading	4	TPM	0.09 - 0.27	0.17	0.18	Internal report OGMB 2001-107	Shell Global Solutions
Aid'operateur	Bitumen truck loading	4	BSF	0.1 - 0.2	0.10	0.12	Internal report OGMB 2001-107	Shell Global Solutions
Aid'operateur	Bitumen truck loading	4	SV	0.81 - 1.7	1.09	1.14	Internal report OGMB 2001-107	Shell Global Solutions
Truck driver	Bitumen truck loading	2	TPM	0.12 - 0.69	0.29	0.41	Internal report OGMB 2001-107	Shell Global Solutions
Truck driver	Bitumen truck loading	10	BSF	0.03 - 1.6	0.24	0.43	Internal report OGMB 2001-107	Shell Global Solutions

Occupation	Source of exposure	Number	Type	Range (mg/m^3)	Geo. Mean	Ari. mean	Ref	Source
Truck driver	Bitumen truck loading	10	SV	0.09 - 1.4	0.38	0.53	Internal report OGMB 2001-107	Shell Global Solutions
Truck driver	Bitumen truck loading	6	16 EPA-PAHs		0.23 $\mu g/m^3$ 8hr TWA	0.31 $\mu g/m^3$ 8hr TWA	Personal Exposure to PAHs in the Refinery During Truck Loading of Bitumen	Deygout 2011[9]
Truck driver	Bitumen truck loading	6	Naphthalene	0.71 – 8.59 ng/m^3	1.89 ng/m^3	2.76 ng/m^3		
Truck driver	Bitumen truck loading	6	B[a]P	2 - 3 ng/m^3	2.2 ng/m^3	2.3 ng/m^3		
Truck driver	Bitumen truck loading	6	BSF	0.10 – 0.25 mg/m^3	0.13 mg/m^3	0.14 mg/m^3		
Truck driver	Bitumen truck loading	6	SV	0.55 1.45 mg/m^3	0.76 mg/m^3	0.80 mg/m^3		
Truck driver	Bitumen truck loading	6	THC	0.65 – 1.70 mg/m^3	0.89 mg/m^3	0.94 mg/m^3		
Plant workers	Bitumen Refinery Plant Operations	82	BSF	0.01-0.26 mg/m^3	0.03	0.05	HRG 2011-2013 Internal Report	Plant Workers
Plant workers	Bitumen Refinery Plant Operations	82	TP	0.03-1.04 mg/m^3	0.22	0.17	HRG 2011-2013 Internal Report	Plant Workers
Plant workers	Bitumen Refinery Plant Operations	26	TOM	0.08-28.8 mg/m^3	1.41	2.77	HRG 2011-2013 Internal Report	Plant Workers

BSM: Benzene Soluble Matter
THC: Total Hydrocarbons
TP: Total Particulates
TOM: Total Organic Matter
TPM: Total Particulate Matters
BSF: Benzene Soluble Fractions
SV: Semi-Volatiles (gaseous fractions)
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 on 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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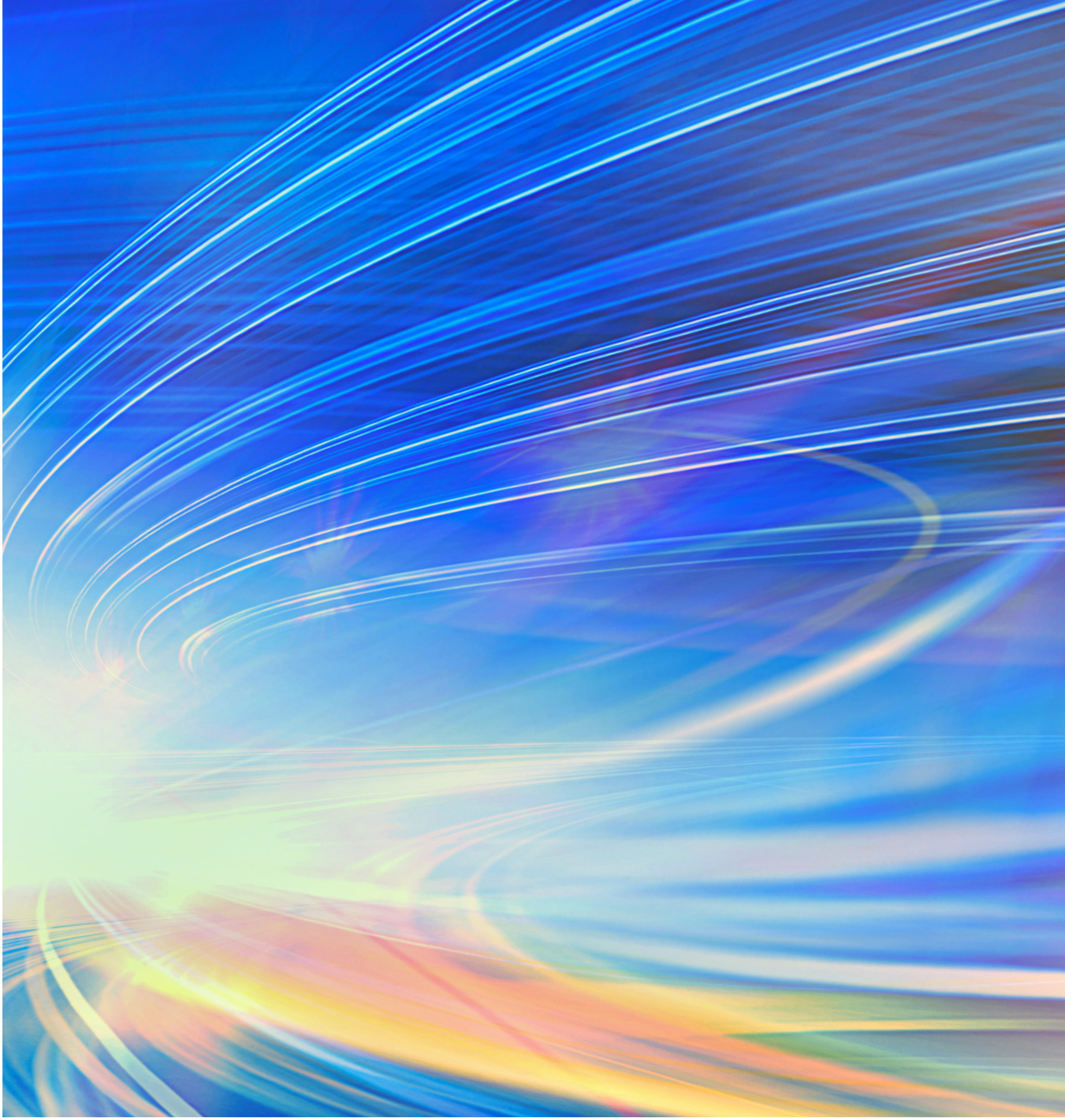

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