bitumens and bitumen derivatives

Prepared by CONCAWE's Petroleum Products and Health Management Groups:

ABSTRACT

This dossier includes information on the manufacture and use of bitumen and its various derivatives. It also summarizes the health, safety and environmental data currently available on bitumens and their derivatives.

KEYWORDS

Bitumen, asphalt, review, toxicology, health.

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APPENDICES

Appendix I BITUMEN ENTRIES IN EINCECS

Appendix II BITUMEN, DERIVATIVES, THEIR MANUFACTURE AND USE

PREFACE

This product dossier is one in a series of 11 on the following major groups of petroleum products:

- Liquefied petroleum gas
- Gasolines
- Kerosines/jet fuels
- Gas oils (diesel fuels/heating oils)
- Heavy fuel oils
- Lubricating oil basestocks
- Aromatic extracts
- Waxes and related products
- Bitumens and bitumen derivates
- Petroleum coke
- Crude oil

These product dossiers are being prepared by CONCAWE to provide, for each major product group, comprehensive information covering:

- Product description, uses and typical properties
- Toxicology, health aspects and fire, explosion and environmental hazards
- Recommended exposure limits
- Advice on handling, emergency treatment and disposal
- Entries in the European Inventory of Existing Commercial Chemical Substances (EINECS) which cover these groups

1. INTRODUCTION

This dossier collates the available health, safety and environmental data on the generic class of petroleum substances known as bitumens and their derivatives.

Bitumens are used mostly for road paving or roofing but find uses in a variety of other applications where waterproofing and adhesion are important required properties.

2. PRODUCT DESCRIPTION

Bitumens are complex combinations of petroleum products, mainly used for paving roads and for roofing but they also have a wide range of other uses. To avoid confusion and misunderstanding that may arise from the use of different terms such as bitumen, asphalt etc., it is essential to be clear about terminology. In this dossier, the following nomenclature is used:

Bitumen

is a black or dark brown solid or semi-solid thermo-plastic material possessing waterproofing and adhesive properties. It is obtained from processing crude petroleum oil and is a complex combination of higher molecular weight organic compounds containing a relatively high proportion of hydrocarbons having carbon numbers greater than C25 with a high carbon to hydrogen ratio. It also contains trace amounts of metals such as nickel, iron or vanadium. It is essentially non-volatile at ambient temperatures and is soluble in carbon disulphide. Bitumen is defined in this way in most parts of the world outside North America.

Natural Bitumens

The term bitumen is also used for "*natural bitumens*" which can occur as natural deposits or as a component of naturally occurring asphalt, in which it is associated with mineral matter. Although natural bitumen may be similar in physical properties to bitumen, it is different in composition and is not covered by this dossier.

Asphalt

refers to a mixture of bitumen (as defined above) with mineral matter such as stone, sand or filler. However, in the USA, asphalt refers to bitumen as defined above.

This dossier does not cover coal tars and pitches which are obtained by the destructive distillation of coals, or mixtures of these with bitumen or bitumen derivatives. They have a declining use in applications such as road paving, roofing etc. There are fundamental differences between the two classes of materials. [1] Chemically, coal tar materials are composed mainly of highly condensed-ring aromatic hydrocarbons. Bitumen contains a much higher proportion of relatively high molecular weight paraffinic and naphthenic hydrocarbons and their derivatives. Differences are illustrated in **Table 1** showing that the content of polycyclic aromatic hydrocarbons (PAHs) in two coal tar pitches are several orders of magnitude greater than those determined in penetration or oxidized bitumens. [2, 3]

Table 1: **Range of polycyclic aromatic hydrocarbon (PAH) levels in bitumens and their fumes compared with coal tar pitch**

	BITUMENS							COAL TAR PITCH	
	PENETRATION GRADES			OXIDIZED GRADES					
Reference	**Walcave* et al** [2]	**Brandt et al** [3]		**Brandt et al** [3]		**NIOSH** [4] **(Roofing bitumens)**		**Brandt et al** [3]	
Bitumen or Condensed Fume (Temperature °C)	**Bitumen**	**Bitumen**	**Condensed Fume (160)**	**Bitumen**	**Condensed Fume (250)**	**Condensed Fume (232)**	**Condensed Fume (316)**	**Pitch**	**Fume (160)**
Number of Samples	**8**	**4**	**4**	**3**	**4**	**2**	**2**	**2**	**2**
PAH (mg/kg)						#	#	all values x 10^3	all values x 10^3
Phenanthrene	0.4-3.5	1.7-7.3	329-842	0.3-2.4	107-382	180-300	53-69	19.8-25.7	210-240
Anthracene	ND	<0.1-0.3	3.6-21	<0.1	4.5-22		4.60-7.31	64-76	
Fluoranthene	ND-2.0	0.4-0.7	14-32	0.2-0.5	13-24	86-97	7.3-10	29-36	76
Pyrene	0.3-8.3	0.3-1.5	26-134	0.2-0.3	15-85	63-70	7.7-9.0	21.3-27.2	44-49
Chrysene	<0.1-8.9	0.5-3.9	91-157	0.8-1.0	33-74	13-25	14-19	11.2-22.7	5.6-11
Benzo(a)enthracene	ND-2.1	0.1-1.1	23-40	0.2-0.3	12-36	7.6-11	5.7-10	20.4-24.5	5.9-12
Perylene	ND-39	<0.1-3.3	1.7-8.1	<0.1-0.2	1.7-15	NR	NR	2.77-3.50	0.12-0.15
Benzofluoranthenes +	NR	ND-0.2	ND-1.6	<0.1-0.1	<0.1-2.6	1.8-5.2	ND-4.0	5.25-60.01	0.38-0.44
Benzo(e)pyrene	<0.1-13	NR	NR	NR	NR	3.6-5.5	1.4-8.2	NR	NR
Benzo(a)pyrene	ND-2.5	0.2-1.8	3.4-6.6	0.4-0.5	5.0-8.5	2.2-2.9	ND-1.9	11.4-15.2	0.55-0.67
Dibenzanthracenes	NR	NR	NR	NR	NR	1.6-1.8	ND	NR	NR
Indino(1,2,3-cd)pyrene	ND-<0.1	NR	NR	NR	NR	2.2-2.7	ND-3.1	NR	NR
Benzo(ghi)perylene	<0.1-4.6	1.7-4.2	6.0-12.0	1.2-2.0	7.0-15	0.8	ND-1.5	3.43-3.53	0.03-0.05
Anthanthrene	ND-<0.1	<0.1-0.1	ND	ND	ND	NR	NR	1.23-1.73	0.01-0.02
Dibenzo(al)pyrene	NR	ND	ND	ND	ND	<0.5	<0.5	ND	ND
Dibenzo(ai)pyrene	NR	ND-0.6	ND	ND-0.3	ND		0.13-0.16	0.13-0.16	ND <0.01
Coronene	ND-1.9	ND-0.4	3.0-11	ND	ND-11	<0.5	<0.5	ND-0.12	ND

NR Not reported
ND Not detectable
* Excluding one sample containing PAH levels approximately an order of magnitude greater than most other samples
+ In Brandt et al paper only Benzo(k)fluoranthene was measured
# Amounts are those in the painting solutions containing 50% bitumen, hence values should be multiplied by 2 for comparison with other groups

2.1. TYPES OF BITUMENS AND BITUMEN DERIVATIVES

The following types of bitumens and derivatives are available to meet the technical requirements of different applications.

2.1.1. Bitumens

There are three main types of bitumens:

- **Penetration Grades**
  are usually produced from crude petroleum oil atmospheric distillation residues by using further processing such as vacuum distillation, thermal conversion, partial oxidation (air rectification/ semi-blowing) or solvent precipitation. A combination of these processes can be used to make different grades which are normally classified by penetration value specifications. They are principally used for road surfacing and in roofing.

- **Hard Bitumens**
  are manufactured using similar processes to penetration grades but have lower penetration values and higher softening points, i.e. they are harder and more brittle. The main use is in the manufacture of bitumen paints and enamels. They one normally classified by a softening point specification and designed by a prefix, H (hard) or HVB (highvacuum bitumen).

- **Oxidized Bitumens (Air Blown)**
  are produced by passing air through a bitumen feedstock under controlled conditions. This produces a higher softening point bitumen with reduced susceptibility to change with temperature and greater resistance to imposed stresses. Applications include use in roofing materials, waterproof papers, electrical components and many other building and industrial products. Classification is normally by both penetration value and softening point specifications.

The European Inventory of Existing Commercial Chemical Substances (EINECS) contains 9 entries which cover bitumens. These entries are listed in **Appendix 1.**

2.1.2. Bitumen Derivatives

Many bitumen derivatives are proprietary formulations and can only be reviewed here in general terms. There are four basic types:

- Cutback Bitumens
- Fluxed Bitumens
- Bitumen Emulsions
- Modified Bitumens

Details for each of the types are given in **Appendix II**.

2.2. MANUFACTURE

The various processes used in petroleum refineries to manufacture bitumens include distillation, air blowing, solvent precipitation (deasphalting) and thermal conversion processes. The products of these processes may be combined by blending operations to meet performance specifications. Ancillary processes are used to manufacture bitumen derivatives. Manufacturing processes are described in more detail in **Appendix II**.

2.3. RELATIVE USAGE

Usage of bitumen and bitumen derivative types varies from country to country, but typically in Europe about 80% of the total is used in roads, about 10% in roofing and the remainder in a variety of other industrial applications.

In road applications, there are considerable variations in local practices but, on average, about 85% are penetration grades, 5% are cut-backs and 10% are emulsions. A few percent of the above types of bitumen and bitumen derivatives are used after modification with polymeric materials.

In roofing applications the average usage is about 50% oxidized bitumens and 50% polymer modified bitumen; the share of bitumen derivatives (liquid roofing) is marginal.

In industrial applications, the average usage is about 50% oxidized bitumen 50% penetration grades with only minor proportions of hard grades.

3. TYPICAL PROPERTIES

Bitumens are normally classified in terms of specification tests which relate properties to the requirements of the intended application. Current specifications differ from country to country and CEN standards are to be introduced in 1993. The properties of bitumens would normally be expected to fall in the following ranges:

Table 2: Physical properties of bitumens.

Property	Units	Method	Penetration bitumen	Hard bitumen	Oxidized bitumen
Penetration at 25°C	0.1 mm	ASTM D 5	40-300	15-40	0-55
Ring & ball softening point	°C	ASTM D 36	30-60	60-75	60-130
Boiling range	°C	ASTM D 2887	>470	>550	>400
Flash point closed cup	°C	ASTM D 92	>230	>250	>250
Viscosity at 60°C	mm^2/s	ASTM D 2171	200-2500	N/A	N/A
Viscosity at 135°C	mm/s	ASTM D 2170	80-400	300-1500	N/A
Viscosity at 200°C	mm^2/s	ASTM D 2170	N/A	N/A	100-1000
Density	kg/m^3	ASTM D 70	1000-1050	1020-1050	1000-1050
TFOT * mass change	%	ASTM D 175	<2.0	<2.0	<2.0

*TFOT = Thin Film Oven Test, 5 hours at 163°C.
N/A = Not Applicable

Properties and tests of bitumen derivatives vary widely with product type and product application.

4. TOXICITY

Terminology found in the published literature to describe the various types of bitumen examined is not consistent. This can give rise to confusion especially when the term Asphalt in the American literature is synonymous with Bitumen in the European literature.

To prevent further confusion ***European terminology only*** is used in the following review on toxicology.

In addition to the studies cited in the following sections, two other extensive reviews have also been published. [5, 6]

4.1. ACUTE TOXICITY

4.1.1. Oral, Skin and Inhalation

No acute toxicity studies relating to these routes have been published on petroleum derived bitumens, though some indications of acute properties can be obtained from sub-chronic and chronic toxicity studies on bitumen or bitumen fumes (see **Section 4.2** and **4.3**) and from acute toxicity studies on related materials. [7, 8]

These data together with information extrapolated from studies on other hydrocarbon mixtures suggest that the acute toxicity of bitumens is likely to be low.

4.1.2. Skin and Eye Irritation

There is only one report acute irritation studies on bitumen or bitumen fume. [9] In one of these studies, fumes derived from heated bitumens were directed into rabbits' eyes. The concentration of the fumes, however, was not specified. Only minor transient conjunctivitis was produced by a single fume exposure and even after multiple exposures only slight *"infiltration"* of the cornea was observed in some cases, which later resolved. In other studies reported by the same authors, bitumen dust or mixed dust applied to the eyes of rabbits and dogs produced inflammation *(blepharo-conjunctivitis, corneitis, episcleritis and iritis).* The changes were more pronounced with bitumen dust than with mixed dust and more marked in rabbits than in dogs. It is uncertain the extent to which these changes were produced by physical irritation. There is also some uncertainty concerning the nature of the materials used in this study and as it was reported in 1913, they may have been natural rather than petroleum-derived bitumens.

Some indication of the acute skin and eye irritancy of petroleum-derived bitumen and bitumen fume can be obtained from reports of chronic studies (**Section 4.3**) and studies on related materials. [7, 8]

It is concluded that the skin and eye irritancy potential of bitumen and its fume is likely to be low.

4.1.3. Skin Sensitization

No data have been reported on commercial bitumens. Two vacuum residues were inactive in guinea pig (Buehler) sensitization assays. [10, 11]

4.2. SUB-CHRONIC TOXICITY

Apart from a study where oral administration of 250 mg/kg of two bitumens to 4 pigs for 71 days produced no effects [12], no 90-day or similar sub-chronic toxicity studies have been reported on bitumen or bitumen fume. However data from chronic studies on bitumen and sub-chronic studies on materials related to bitumen do provide some indication of likely effects.

In these studies no systemic effects have been reported, the only effects observed being skin irritancy in dermal studies and lung irritation in inhalation studies.

It is concluded that the sub-chronic toxicities of bitumen and bitumen fume are likely to be low and most probably restricted to irritant effects on the skin or in the lungs, depending on the route of exposure.

4.3. CHRONIC TOXICITY

The main aim of the chronic toxicity studies conducted on bitumen has been to investigate possible carcinogenicity. No systemic effects have been noticed, but chronic irritancy effects have been reported in the skin and lungs following dermal exposure or fume inhalation.

4.3.1. Carcinogenicity

Long-term studies have been performed on various types of bitumen as identified in **Section 2.1.1**, but authors have used a variety of terms to describe the materials they have tested. For the purposes of this document the following terms are used:

Penetration bitumens
include steam-refined bitumens and road bitumens

Hard bitumens
include bitumen paint

Oxidized bitumens
include air-blown, air-refined and roofing bitumens

Thermally-cracked bitumens
considered to include *'cracked residue bitumens.'*

Two main forms of exposure must be considered in the assessment of the carcinogenicity of bitumen: skin contact with bitumen itself and inhalation of the fumes generated when bitumen is heated. Limited skin contact with condensed fume might also be a possibility in some situations.

4.3.1.1. Dermal Carcinogenicity Studies

A summary of the dermal carcinogenicity studies conducted in mice are shown in **Table 3**.

Table 3: Summary of dermal carcinogenicity studies in mice with different bitumen grades

Bitumen Description	Treatment	Duration	Skin Tumour Incidence	Reference
Penetration Bitumens				
1 Steam-Refined	Undiluted (heated)	21 months	5 in 63 mice (21 survived)	Simmers 1965 [13]
4 Road Bitumens	Diluted with acetone 2x weekly (concentration unspecified)	2 years	4 in 200 mice (All 4 bitumens) 2% Highest 4% Lowest 0%	Hueper and Payne 1960 [14]
4 Penetration Bitumens	40% in benzene 1x weekly	19 months	4 in 163 mice (All 4 bitumens) 2.5% Highest 4.8% Lowest 0.6%	Kireeva 1968 [15]
8 Penetration Bitumens	10% in Benzene 2x weekly	>81 weeks	6 in 218 mice (All 8 Bitumens) 2.7% Highest 7% Lowest 0%	Walcave et al 1971 [2]
1 Penetration Bitumen	30% in mineral oil 2x weekly	24 months	0 in 50 mice	McGowan et al 1992 [16]
Hard Bitumens				
1 Bitumen Paint	60% bitumen in mineral spirit 1x weekly	30 weeks	1 in 40 mice (2.5%)	Robison et al 1984 [17]
Oxidized Bitumens				
1 Air Blown Bitumen	Undiluted (heated) 1 to 3x weekly	21 months	1 in 50 mice (only 10 survived)	Simmers 1965 [13]
1 Air Blown Bitumen	90% in toluene 3 x weekly	2 years	9 in 20 mice (45%)	Simmers 1965 [13]
1 Roofing Bitumen	Diluted with acetone 2x weekly (Concentration unspecified)	2 years	1 in 50 mice (2%)	Hueper and Payne 1960 [14]
1 Roofing Bitumen	50% in toluene 2x weekly	80 weeks	0 in 50 mice (0%)	Emmett et al 1981 [19]
1 Roofing Bitumen	50% in acetone/ cyclohexane 2x weekly	2 years	3 in 30 mice (10%)	Sivak et al 1989 [20]
Mixed Penetration and Oxidized Bitumens				
Mixture of Six Air Blown and Steam-Refined Bitumens	Diluted with benzene 2x weekly (Concentration unspecified)	More than 54 weeks (Not specified)	17 in 68 mice (25%)	Simmers et al 1959 [21]
Thermally-cracked Bitumens				
2 "*Cracking-Residue*" Bitumens	40% in benzene 1x weekly	19 months	9 in 49 (18.4%) 4 in 42 (9.5%)	Kireeva 1968 [15]

Undiluted Bitumens

Both penetration and oxidized bitumen have been applied undiluted to mouse skin by heating them sufficiently to make them mobile. [13] Although some skin tumours were induced in such studies, the data may not be reliable since it is possible that repeated burns may have been responsible for cancer induction. Other factors such as poor survival, self-inflicted skin damage and poor skin contact further limited the reliability of the findings.

In addition to the mouse studies, four penetration bitumens applied twice weekly in heated form to the ears and back of 6 rabbits for 2 years failed to induce skin cancer. [14]

There is thus no reliable evidence that undiluted bitumens are carcinogenic.

Solvent dilutions of Bitumen

All other dermal studies have involved solvent dilutions of bitumens.

Penetration Bitumens

Four studies have been reported on a total of 17 penetration bitumens from different sources, diluted with acetone, benzene. [2, 13, 14, 15, 16] The average tumour incidence within these studies ranged from 2-2.7% and the tumour incidence with individual bitumens ranged from 0-7%. This implies that penetration bitumens have little or no carcinogenic activity even if diluted with a solvent.

Hard Bitumens

There was only one skin carcinogenicity study available on a single hard bitumen [17] and this is of limited reliability owing to its short duration (30 weeks). However, as only one skin tumour was induced in 40 mice, it is unlikely that the carcinogenic activity of this bitumen was more than weak. Initiation-promotion studies reported in the same paper were inconclusive, although the authors claimed that they demonstrated carcinogenic activity, this was later contested. [18]

Oxidized Bitumens

Four studies were available on solvent dilutions of single oxidized bitumens. These showed greater variation then penetration bitumens. Two of the studies [14, 19] showed essentially noncarcinogenic activity (0 or 2% tumour incidence), whereas the other two [13, 20] showed weak (10% tumour incidence) or clear (45% tumour incidence) activity. The report showing clear activity [13] is, however, of limited reliability owing to the small number of mice used and the severity of the treatment (3 times weekly as a 90% solution in toluene).

It is possible that the toluene vehicle rnight have produced severe skin irritancy under these conditions and this was confirmed by observations of hair loss, "*scaliness and skin thickening"* in the vehicle control animals. The finding of a single papilloma in 8 toluene control mice autopsied in this study reinforces this concern and implies that the tumour incidence reported may not have been solely due to bitumen. Hence, although the response to oxidized bitumens diluted with solvents is variable, it is unlikely that they have more than weak carcinogenic activity.

Mixed Bitumens

A single study was conducted [21] on a mixture of six penetration and oxidized bitumens diluted with benzene, in which a 25% incidence of skin tumours was reported with a latency of 54 weeks. This study is difficult to interpret as it is uncertain whether the activity reported was due to penetration or oxidized bitumens. However it does imply that some bitumens cut back with solvent have at least weak carcinogenic activity.

Thermally-Cracked Bitumens

It was reported [15] that two *"cracked residue"* bitumens derived from destructive distillation produced a higher skin tumour incidence than penetration bitumens. This suggests that thermally-cracked bitumens may have slightly greater carcinogenic potential than penetration bitumens; however, it should be recognized that the definition of the materials tested by Kireeva was uncertain.

4.3.1.2. Subcutaneous and Intramuscular Studies

These studies are detailed in **Table 4**. In all studies in which bitumen was administered by subcutaneous or intramuscular injection, induction of local sarcomas did not exceed 13%. It has been shown that subcutaneous or intramuscular injection of substances does not give a reliable prediction of carcinogenic activity particularly where multiple injections are given and tumour incidence is low. [22] Where bitumens were injected in a molten state the further complication of tissue overheating has to be considered. This is likely to be greater with oxidized bitumen as the softening point is higher.

In addition to these considerations human exposure to bitumen does not occur by these routes. Hence the induction of low incidences of sarcomas by such procedures is not relevant to an assessment of the carcinogenic risk of bitumen to man.

Table 4: Carcinogenicity testing bitumens by sub-cutaneous (s.c.) or intramuscular (i.m.) injection.

Bitumen Description	Species	Treatment	Duration	Tumour Incidence (Sarcomas) at treatment site	Reference
Penetration Bitumens					
1 "*Steam-Refined*"	Mice	1 or 2 s.c. of molten bitumen	23 months *	0 in 50	Simmers 1965 [13]
4 "*Steam distilled*" Bitumens	Mice	2x weekly i.m. of 50% in tricaprylin for 3 weeks	2 years	3 in 200 (1.5%)	Hueper and Payne [14]
4 "*Steam Distilled*" Bitumens	Rats	2x weekly i.m. of 50% in tricaprylin for 6 weeks	2 years	13 in 120 (11%)	Hueper and Payne [14]
Oxidized Bitumen					
1 "*Air-refined*" Bitumen	Mice	1 or 2 s.c. of molten Bitumen	23 months	5 in 50 (13% of survivors)	Simmers 1965 [13]
Mixed Penetration and Oxidized Bitumens					
Mixture of 6 air-blown and steam-refined Bitumens	Mice	2x weekly s.c. 1% suspension in olive oil for 41 weeks then 1x weekly	not specified (>41 weeks)	8 in 62 (13%)	Simmers et al 1959 [21]

4.3.1.3. Inhalation Studies

Inhalation studies have only been carried out on an oxidized bitumen and a mixture of six penetration and oxidized bitumens.

In studies on an oxidized bitumen 65 Bethesda black rats and 30 Strain - 13 guinea-pigs were exposed to bitumen fumes for five hours per day on four days per week over two years. [14] Fumes were generated by volatilizing 2-10 grams of air-blown bitumen per day from a dish heated to 250 to 275 °F (120 to 135°C) inside the exposure chamber. The concentration of the fume was not stated; it was mentioned that an unspecified volume of cooled air was passed into the chamber to maintain the temperature at 75°F (24°C). None of the animals developed lung cancer although some rats and guinea pigs were diagnosed as having *"extensive chronic fibrosing pneumonitis with peribronchial adenomatosis which was associated in rats with squamous cell metaplasia of the bronchial mucosa".* These histological changes were not judged to be cancerous or pre-cancerous in nature.

In the first of two inhalation studies reported on a mixture of six penetration and oxidized bitumens, [23] 20 C57 black mice were exposed for 30 minutes each day on five days per week over 17 months to a mixed bitumen/water droplet aerosol of unstated concentration. Only a single lung adenoma arose, but as benign tumours of this type occasionally occur spontaneously in animals of this strain [24] and as no malignant respiratory tract tumours arose, no carcinogenic response was indicated. Other histological changes observed in the lungs were minimal, these included occasional incidences of pulmonary congestion, bronchitis and pneumonitis.

In the second inhalation study, 30 C57 black mice were exposed to mixed bitumen fumes for 6-7.5 hours each day on five days per week over 21 months. The fumes were generated by heating the pooled bitumens to 250°F (120°C). They were forced through the exposure chambers with a fan but no indication of flow rate or fume concentrations was given. Only a single lung adenoma was found, with no other benign or any malignant respiratory tract tumours. Again this provided no indication of cancer induction. Signs of pulmonary toxicity were more marked than in the first study, the histological changes including bronchitis loss of bronchial cilia, epithelial atrophy and necrosis in addition to pneumonitis.

The levels of exposure to bitumen furies in the above studies and in the study by Heuper and Payne in 1960 on oxidized bitumen, although not specified, were irritant to the respiratory tract and might in some cases be regarded as approximating to a maximum tolerated dose. Hence, despite the failure to monitor exposure levels adequately in the studies described, the dose levels employed were probably sufficient to conclude that it is unlikely that bitumen fumes have any carcinogenic effect in animals by the inhalation route.

4.3.1.4. Skin Application of Condensed Fumes of Oxidized Bitumen

The carcinogenic effects of condensed fumes of bitumen by skin painting in mice of the C3H/HeJ and the CD-1 strains have been reported by NIOSH. [4] Condensates from fumes generated at 232°C from two types of roofing asphalt (bitumen) were applied as 50% weight/volume solutions in 50/50 cyclohexane/acetone to the skin, twice weekly for up to 72 weeks. In some animals the skin was also exposed to UV light. These studies demonstrated that the test solutions containing condensed bitumen fumes were carcinogenic to the skin of mice both in the presence and absence of UV light (UV light had a slight inhibitory effect). The C3H/HeJ mice were clearly more sensitive, with tumour incidences in the absence of UV light ranging from 89% to 96% with mean latencies (time of tumour appearance) from 40 to 51 weeks, compared with tumour incidences in CD1 mice of 16 – 43% with mean latencies of 52-60 weeks.

In the CD1 mouse the lower temperature fume was clearly less active than the high temperature fume (18% tumour-bearing animals compared with 47% for one fume and 29% compared with 43% for the other fume). No such differences were apparent in the more sensitive C3H/HeJ mice.

A further investigation was reported [20] of the skin carcinogenic activity of condensed bitumen fume generated at 316°C from a roofing asphalt (bitumen) on groups of 30 male C3H/HeJ and Sencar mice. In addition to testing bitumen fume condensate, five fractions of this were prepared by liquid chromatography and tested on C3H/HeJ mice. The whole fume condensate was applied to the skin as a 50% solution in 50/50 cyclohexane/acetone twice a week, the other fractions being tested at concentrations stated to be in proportion to their presence in the condensate.

With the fume condensate, findings with C3H/HeJ mice were similar to those of the NIOSH study with 20 out of 30 mice developing carcinomata. With Sencar mice a slightly lower incidence was obtained with 14 out of 30 mice developing carcinomats. The main carcinogenic activity of the condensate in C3H/HeJ mice appeared to be present in two of the fractions (B and C), the latter being more active. No synergism between the fractions was detected. [CONCAWE noted that although the authors drew attention to the presence of other ingredients in these fractions, both contained polycyclic aromatic compounds (PACs) and these may have been responsible for the activity of the bitumen fume condensates].

Both studies on bitumen fume condensates clearly demonstrated their carcinogenicity to the skin under the test conditions described. However, it is not clear why the fume condensate was diluted 1:1 with a mixture of cyclohexane and acetone; this may well have potentiated the carcinogenic effect by making PACs more bio-available. The temperature of fume generation is also important as it affects the 3-7 ring PAC content of the fume. The temperature of 316°C employed in both these studies was clearly in excess of that recommended for all types of bitumen and was stated to represent the high overheat kettle temperature in the field. As the temperature of bitumen which most workers handle is likely to be below this, it is uncertain how relevant to man the data are. In any event, the exposure resulting from painting the skin with fume condensate under these conditions is grossly in excess of that which might occur in the lungs, due to fume inhalation, or on the skin, resulting from the limited amount of fume condensation that might occur on the skin or clothing of workers. For these reasons, it is unlikely that skin carcinogenicity studies on fume condensates give a realistic indication of the practical carcinogenic hazard of bitumen or its fumes.

Summary of Carcinogenicity Data

Carcinogenicity studies have been carried out on penetration (steam-refined), hard, oxidized (air blown) and thermally-cracked bitumens. From these studies the following conclusions can be drawn:

- There is no evidence that undiluted bitumens of any type are carcinogenic. The few studies conducted are unreliable due mainly to the high temperatures that were used to make the bitumens sufficiently mobile to apply to animals.

- There is evidence that some bitumens, diluted with solvent, are carcinogenic, though many are only weakly so. Data on bitumens diluted with solvent can only be considered relevant to human exposure in situations where cut-back bitumens are used at ambient temperatures.

- Condensed fumes from roofing bitumens heated to 232 or 316°C when tested as solutions in organic solvents caused skin cancer in mice. However, there were a number of factors in these studies which indicated that the degree of exposure of the experimental animals to the carcinogenic substances in these fume condensates, was likely to be grossly in excess of that likely to occur in man from bitumen exposure. These studies were therefore not considered to give a realistic indication of the carcinogenic risk to man of bitumen or its fumes.

- Despite the shortcomings of the animal inhalation studies conducted on fumes from heated, air-blown or mixed penetration and air-blown bitumens, they do suggest that the inhalation of such fumes is unlikely to result in cancer of the respiratory system.

4.3.2. Genotoxicity

Mutagenicity

In Ames tests, [25] a dimethylsulphoxide (DMSO) extract of road tar and DMSO solutions of volatiles generated in the laboratory at 550, 350 and 250°F appeared to have weak mutagenic activity in the presence of a metabolic activation system (S9). [It is unclear from the product description of "*road tar*" whether or not it contained coal-derived materials]. On the other hand it has been reported [26] that DMSO extracts of three bitumen samples were inactive in the Ames tests, as were extracts of airborne particulates collected during road paving operations. It was suggested that components of the bitumen might be having inhibitory effects on mutagenicity despite the microsomal (S9) fraction being increased five-fold in this study in an attempt to circumvent this.

Components of "*asphalt tar*" inhibited benzo(a)pyrene mutagenicity and fractionation studies were conducted which indicated that the polycyclic aromatic hydrocarbon (PAH) fraction was responsible for the inhibitory effect. [27] [CONCAWE noted that the nature of the material tested is not clear].

It has been reported that, whereas a petroleum pitch with a high PAH content (e.g. 1.5% benzo(a)pyrene) was active in the Ames assay when a DMSO extract of it was examined using elevated S9 levels, a penetration bitumen with a much lower PAH content was inactive under the same test conditions.

Four samples of bitumen-based paints, containing approximately 60% bitumen cut back with mineral spirit, were reported to be inactive in Salmonella assays 17 both in the presence or absence of S9 mixture; whereas four coal-tar paints were clearly mutagenic in the presence of S9 when tested under the same conditions. [28]

Marginally positive findings have been reported [29] with DMSO extracts of *"whole asphalts"* (roofing and paving bitumens), examined in a modified Ames assay [30] involving an elevated S9 level (Mutagenicity Index (MI) < 1.5). Fume condensates, derived from heating those materials to temperatures above 450°F (232°C), were moderately active (MI 4.0-8.8). Fumes generated from coal tar pitch in the same way were over 1000 times more active. When a paving bitumen was heated to a temperature more representative of that found in practice 325°F (163°C) very little fume was generated and its MI was much lower. This questions the relevance of data obtained from high temperature fume generation.

A further study of a penetration bitumen was negative in a modified Ames test. [16]

Other genotoxic effects

When DMSO extracts of a penetration bitumen and petroleum pitch were administered intraperitoneally to rats, no in vivo DNA damage was seen in the liver using alkaline elution and a fluorimetric assay of DNA unwinding. [28] The meaning of these results is unclear but the negative result with the petroleum pitch extract implies that the test is insensitive to complex hydrocarbon mixtures.

However, on the basis of studies using the ^{32}p-post-labelling technique it was claimed that repeated skin applications of bitumen solution gave rise to an accumulation of DNA adducts in the skin and to a lesser extent in the lungs. [31] The same group of workers [32] reported that treatment of human skin in short-term organ culture gave rise to similar DNA adducts.

Genotoxicity conclusions

In most mutagenicity assays conducted, bitumens have given negative or marginally positive findings. Although there is some evidence that high temperature bitumen fume may have moderate mutagenic activity in a modified Ames test, it is questionable whether the fumes generated during normal operations have more than weak activity. Caution should be exercised in drawing parallels between mutagenicity in the Ames assay and the carcinogenic properties of complex hydrocarbon mixtures such as bitumen, since many non-carcinogenic PAHs give positive results with this assay, [33, 34] However, a modified assay which has been described [29] gives a better distinction between carcinogenic and non carcinogenic PAHs.

In some postlabelling studies weak DNA binding has been seen with some bitumens, but whether the circumstances under which these have been produced are relevant to human exposure is uncertain. These studies involved the application of bitumen in a solvent vehicle and hence are subject to the same criticism as animal carcinogenicity studies employing cut-back bitumens.

The ^{32}p-postlabelling studies show that the bitumen tested do contain genotoxic components. In neat bitumen the physical properties of the bitumen may significantly inhibit the bioavailability of any potentially genotoxic components. ^{32}p-postlabelling studies on bitumen fume have not been carried out and therefore the DNA adduct forming potential of this material is not known.

5. HEALTH ASPECTS

5.1. HUMAN EXPERIENCE

Apart from thermal burns, acute effects of bitumen or its fumes have only occasionally been reported. Health authorities in one state of the USA reported 14 cases of dermatitis. [35] In Norway, symptoms such as fatigue, reduced appetite, laryngeal/pharyngeal irritation, cough and eye irritation have been reported. [36] However, it is likely that these effects were largely due to the solvents used, rather than to bitumen. Most published papers on human exposure to bitumen have addressed the possibility of carcinogenic risk, these are summarized in **Table 5**. Concurrent or prior exposure to coal tar products, especially coal-tar pitch is a confounding factor in many of these studies. As coal-tar pitch contains very much higher PAH levels than bitumen, any prior or concurrent exposure is likely to outweigh the effects of bitumen. Smoking is another compounding factor where lung-cancer is concerned and drinking habits may be relevant to gastrointestinal cancer and liver effects. In the studies reported some information on coal-tar pitch is sometimes given but usually no account has been taken of smoking or drinking habits (mainly due to study design). In roofers and building workers, asbestos exposure is also a possible confounding factor in relation lo lung cancer.

None of the occasional cases of skin cancer (including scrotal cancer) reported in early studies [37, 38] have been attributed to bitumen exposure. Two general surveys of workers exposed to bitumen have been reported. [35, 40] Whereas the former [35] reported no health effects the latter [40] claimed an association between a significant increase in general cancer incidence and bitumen exposure. These general studies based on company data, insurance claims and census data are of limited value, as they are imprecise on occupational data and do not take exposure to other materials such as coal-tar pitch into consideration. The lack of any significant increase in any specific type of cancer, however, implies that bitumen exposure in general does not present any clear health risk.

Two studies on workers employed in the manufacture of bitumen did not indicate an increase in cancer risk or other health hazard. [32, 41] Although these studies are of limited value due to their design, they do imply that little health hazard exists in the manufacture of bitumen. A general review of 100 published and unpublished reports on petroleum industry employees by [42] would seem in keeping with this, as a significant lung cancer deficit was reported together with the absence of any elevation in skin cancer.

Four studies were available on roofers and building insulators. In three of these, significant increases in lung cancer were reported, with an increasing laryngeal cancer in one study. [43, 44, 45] In the fourth study a non-significant increase in oral cancer was reported. [46] Even if the limitations of individual studies are taken into account there would seem to be an increased risk of lung cancer among roofers and building insulation workers. However as substantial use of coal-tar pitch in roofing and building insulation has taken place in the past [43] it is more likely that this is responsible for the incidence than bitumen. This would seem to be confirmed by the absence of any increased incidence in the 9-19 year cohort where bitumen fume exposure is likely to have predominated.

Two studies were available on road maintenance workers, one a proportional mortality ratio study [47] and the other a well-conducted cohort mortality study. [48] No increase in overall cancer or site specific cancer that might be related to bitumen fume exposure was detected in either study. This implies an absence of lung cancer risk due to bitumen fume exposure in road maintenance workers.

In addition to papers on general bitumen exposure and on specific occupations, an increase in lung cancer incidence has been reported [39, 49] in Danish workers exposed to mastic asphalt in flooring and road work. These publications referred to the same cohorts, the first covering 1959-1984 and the second 1959-1986. There was some discrepancy between the two papers as a total of 27 lung cancer cases were reported in the first study, whereas only 25 were reported in the second. The second paper provided no new information and hence comments are made only on the more detailed first paper. Only one sub-cohort (III) (born after 1930) was reported to have had no exposure to coal-tar and this contained only 3 cases of lung cancer. Furthermore it is unclear what denominator was used for the incidence as only those workers over 40 years of age in this sub-cohort were included in the analysis (the age range was from 15 to 54 years). The same criticism applied to the next sub-cohort where coal-tar exposure was described as possible (age range 15 - 64 years). Observations that all three lung cancer cases in the *"no coal-tar exposure*" group were smokers and that their birth dates were only just over the 1930 limit, throws further doubt on the reliability of the findings. It has been subsequently demonstrated that coal tar pitch was used in the industry in Denmark up to 1970. Hence coal-tar exposure is a possible cause for the increase in lung cancer incidence reported in these mastic asphalt workers and evidence of increased smoking is a possible additional confounding factor.

In conclusion there is no evidence that human exposure to bitumen or its fumes in manufacturing processes or in road use results in any cancer risk. Where there is some evidence of an increased risk of lung cancer among roofers, building insulators and mastic asphalt workers, concurrent or previous exposure to coal tar products has also taken place and may therefore have been responsible.

Table 5: Human epidemiological studies on bitumen

Population examined	**Incidence in bitumen exposed group, SMR and control incidence when appropriate**	**Exposure to coal-tar pitch**	**Smoking habits**	**Reported conclusions**	**Reference**
Construction workers (case study)	2 cases of scrotal cancer following 13 or 20 years exposure	One known, one suspected	Not relevant	No evidence of bitumen related effect claimed	Oliver 1908 [37]
3,753 cases of skin cancer (case study)	1 case exposed to natural bitumen 2 cases exposed to bitumen paint	No exposure Exposure reported in both cases	Not relevant Not relevant	Not relevant No evidence of bitumen related effect claimed	Henry 1947 [38]
96 workers at bitumen plant (up to 40 years) (case report)	1 case of bronchial cancer	None likely	Unknown	No evidence of bitumen related effect claimed	Hoogendam 1962 [41]
462 bitumen workers from 25 oil refineries (minimum exposure 5 years, mean 15 years) (Cross sectional health survey)	2 cases of skin cancer (basal cell epithelioma) (4 cases in control group) No difference from the 379 workers in the control group was reported	None likely	No data	Bitumen reported not to pose a significant health hazard	Baylor and Weaver 1968 [35]
31 companies in road construction roofing and haulage contractors plus insurance claims (health status report)	No increase in health effects due to Bitumen	No data	No data	Bitumen reported not to pose a significant health hazard	Baylor and Weaver 1968 [35]
5939 American trade union members who have used coal-tar pitch and bitumen for insulating roofs and foundations, minimum membership 9 years (cohort mortality study)	Cancer death rate (Compared with control) 9-19 yr. membership cohort: 86 deaths (control 80) SMR 107 20+ yr. membership cohort 315 deaths (control 217) SMR 145 Lung cancer incidence 9-19 years SMR 92 20-29 years SMR 152 30-39 years SMR 150 40+ years SMR 247	Exposure to coal tar pitch predominated in earlier years whereas asphalt exposure predominated in later years	No data	Roofers (exposed to coal-tar pitch and bitumen) had elevated death rate from lung cancer (and other cancers). Related by the authors to benzo(a)pyrene exposure	Hammond et al 1976 [43]
2000 white male roofers (estimated from census of 1 in 50) (aged 20-64)	6 lung cancer deaths and 5 incidence cases SMR 496	No data	No data	Excess incidence attributed to PAH exposure	Menck and Henderson 1976 [44]
Roofers and slaters	Non-significant increase in oral cancer	No data	No data		Decoufle et al 1977 [46]
Building insulators	High mortality rate Laryngeal cancer SMR 270 Bronchial and lung cancer SMR161	No data	No data		Milham 1982 [45] (Cont'd …)

1570 deaths in California Department of Transportation (327 highway maintenance workers) Proportional Mortality Ratio Study	No significant PMR's for any cancer site in Highway workers (PMR = 98 for lung cancer)	No data	No data		Maislish et al 1988 [47]
4849 male highway maintenance workers (at least 1 year employment) (cohort mortality study)	Overall no significantly raised SMRs for any cancer site. All cancer SMR 83 Respiratory tract SMR 69 Gastro-intestinal SMR 82 Urinary tract SMR 92 (Elevation of leukaemis in workers with 30-90 years employment SMR 425 and of urinary tract cancer in those with 40-49 years latency).	Stated not to have been used for 50 years	No data	Leukaemia cluster may not reflect occupational exposure and the raised urinary tract cancer incidence is of uncertain aetiology No evidence of bitumen related effects claimed.	Bender et al 1989 [48]
479 mastic asphalt workers (3 sub-cohorts): I 194 workers born up to 1919 (40-89 years) II 129 workers born 1920-1929 (15-64 years) III 356 workers born 1930 onwards (age 16-54 years) 1/3 flooring work 2/3 road work (Cohort Mortality Study) Data from 1959-1984	Lung cancer incidence reported to be significantly increased: I 18 cases SMR 302 II 6 cases SMR 392* III 3 cases SMR 857* * Calculated only on proportion of cohort greater than 40 years of age. Significant increases in cancer in the mouth oesophagus and rectum also reported (only in I)	Sub-cohorts: I *"likely coal-tar exposure"* II *"Possible coal-tar exposure"* III *"no coal-tar exposure"*	Evidence presented that workers smoked more than general population	Bitumen fume exposure claimed to have contributed to the cancers observed	Hansen 1989 [39]
1320 workers in asphalt industry compared with 43,024 unskilled men in causes of mortality. Data from census records and Death Register. (Historical Cohort Study)	Significant increase in overall cancer in workers over 45 with at least 5 years latency. SMR 159 No significant increase for respiratory bladder and digestive tract cancers. Significant increase for brain cancer SMR 500 (3 cases)	No data	No data	Some effect of bitumen was claimed although increases in incidence of respiratory bladder and digestive tract cancers were not significant	Hansen 1989 [40] (Cont'd …)

679 mastic asphalt workers, 3 sub-cohorts I 194 workers age 40-89 II 129 workers age 15-74 III356 workers, age 15-64 (grouped by birth date) (Cohort Mortality Study)	Cancer Incidence 15-40 years SMR 0 40-64 years SMR 304 65-89 years SMR 178 Lung cancer 40-89 years 25 cases SMR 229 Non-pulmonary cancer 40-89 years 37 cases SMR 200	Sub-Cohorts: I "*Likely coal-tar exposure*" II "*Possible coal-tar exposure*" III "*No coal-tar exposure*"	Evidence given that workers smoked more than general population	Bitumen fume inhalation may have contributed to cancer and respiratory disease	Hansen 1991 [49]

5.2. BIOLOGICAL MONITORING OF HUMAN EXPOSURE

A few biological monitoring studies have been conducted in order to assess human exposure to PAHs resulting from bitumen road surfacing operations.

It has been reported that increased levels of hydroxypyrene (a metabolite of pyrene) were present in the urine of workers before and after working at a creosote-impregnating plant and in workers at a majority of nine road-working sites where blends of bitumen and coal-tar were being used. [50] In contrast, no increases in hydroxypyrene levels were found in the urine of workers at a road-working site where bitumen only was being used.

An increase in urine mutagenicity (assessed by the Ames test) in non-smoking workers exposed to bitumen in road-paving operations has also been reported. [51] However, the levels present in bitumen exposed cigarette smokers were not significantly different from non-exposed smokers, the latter having higher mutagenicity levels. In the same study thioether and d-glucaric acid levels were also monitored in the urine. Thioethers appear in the urine when glutathione or other SH-bearing molecules combine with genotoxins in the liver as part of the detoxification process, while increased release of d-glucaric acid can be taken as evidence of increased liver mixed function oxidase activity. No significant increases were seen in either parameter in association with bitumen exposure.

Workers exposed to bitumen fumes in road-laying operations failed to show increased thioether concentrations in their urine, but that cigarette smokers did. [52]

Whereas measurements such as hydroxypyrene levels in urine are claimed to be specific for PAH exposure (but not carcinogenic PAC exposure), others such as urine mutagenicity, thioether excretion and d-glucaric acid excretion are non-specific. The latter are hence more likely to be affected by dietary mutagens and carcinogens, alcohol consumption and other environmental factors, particularly if the control group is not carefully matched with the exposed group. This casts some doubt on the relevance of urine mutagenicity in non-smokers reported by Pasquini et al since they used office workers as a control group for bitumen workers. [53]

Summary:

In the three studies on road workers employing four different biological parameters, only one of questionable relevance showed any increase. In three of these four parameters exposure to PAHs from sources other than bitumen fumes gave positive findings. This implies that human exposure to PAHs in road-paving operations employing bitumen, is low.

Even if positive findings are obtained in the future with assays of this type with other bitumen exposures, it would not imply that a human risk exists, since it has been emphasized by [54] that such measures cannot be used to calculate carcinogenic risk.

5.3. HEALTH HAZARDS

The research world-wide on possible adverse human health hazards following exposure to bitumen, is limited. Most investigators question the possible links between bitumen and cancer. There is a great deal of uncertainty regarding the degree of exposure necessary to cause such health effects.

5.3.1. Inhalation

Inhalation of bitumen fumes may cause irritation of the respiratory tract. After long term exposure to high concentrations of fume, chronic bronchitis with reduced (PEF) and, possibly, other respiratory disorders may result. It is uncertain whether the irritant effect from inhalation of fumes also may influence the gastrointestinal tract.

There is little evidence that lung cancer can result from inhalation of bitumen fumes.

Where cut-back bitumens are handled, acute or longer-term exposure to fumes of the carrier material (white spirit, gas oils or kerosine) may result in irritation to the respiratory tract or *"organic solvent syndrome".*

Spraying of emulsions can result in the generation of a mist. Whether this presents a hazard will depend on particle size but it is unlikely to be within a respirable range (<5 µm).

In confined vapour spaces above heated bitumen in storage tanks, hydrogen sulphide may present a potential hazard.

5.3.2. Ingestion

The physical nature of bitumens and derivatives makes their ingestion unlikely during normal use. However, in the event that accidental ingestion does occur, some irritation of the gastrointestinal tract may arise and result in vomiting with the potential associated danger of aspiration.

5.3.3. Aspiration

Aspiration of liquid into the lungs, either directly or as a result of vomiting after ingestion, is only a possibility with cutback bitumens and emulsions and will not occur with other bitumens and derivatives. Aspiration could give rise to a rapidly developing and potentially fatal chemical pneumonitis depending on the other components present with the bitumen.

5.3.4. Skin Contact

Most bitumens and derivatives are handled hot, and the main danger is from thermal burns.

Cutbacks may sometimes be handled at lower temperatures where prolonged and repeated contact may occur. In addition to causing skin irritation, it would be prudent to assume that such contact may present a potential carcinogenic hazard, particularly under conditions of poor skin hygiene. The situation may be exacerbated by ultraviolet rays in sunlight.

Exposure of the skin to high concentrations of bitumen fumes may also cause skin irritation since there may be condensation onto the skin.

5.3.5. Eye Contact

A hot bitumen splash may cause serious eye injury. Direct contact with cutback, emsulsions and small particles of cold hard bitumens may cause eye irritation.

Irritation of the eyes from exposure to bitumen fumes is also reported among asphalt workers. Although this rarely causes any severe damage to the eyes, it may be a considerable problem to the asphalt workers.

5.4. HEALTH ASPECTS ASSOCIATED WITH SPECIFIC APPLICATIONS

5.4.1. Hot Mixes

Exposure to fume can occur during loading, transport and application of the finished product. Here it is essential to control aggregate temperature such that the product is not overheated. (The 1990 EAPA conference recommends that 160°C should be the maximum production temperature for normal products). During the application procedure there is a limited exposure to fume, but again this can be minimized by ensuring that the initial product is not overheated.

5.4.2. Surface Dressing

Exposure to fume occurs in the immediate vicinity of the spray system (normally a purpose built tanker). The main operatives at risk are the spray bar operator and the driver of the aggregate distributor. Modern equipment trends either eliminate the need for a spray bar operator, or provide a protective ventilated enclosure. In the case of the aggregate distributor driver, modern trends in equipment provide an enclosed ventilated environment:

Where older equipment is used an air hood can be used by both spray bar operative and aggregate distributor driver.

In addition cleaning equipment after spraying has a potential for skin contact.

5.4.3. Recycling

Rejuvenating agents which may be high in PACs are sometimes used in conjunction with asphalt recycling. Such agents would not normally be classified as bitumens and appropriate advice should be sought.

The old asphalt layer may contain coal tar, a coal tar creosote or materials such as reclaimed tyre rubber or PVC, which when heated produce hazards associated with the fumes of these products.

A fume hazard may exist in hot recycling processes both in situ and in plant, where overheating of the old asphalt pavement can cause fumes.

In cold recycling, emulsion sprays may be generated when unenclosed spray systems are used as part of the mixing processes (see **Section 5.3.1**).

5.4.4. Roofing

Exposure to fumes (and sometimes mineral dust) may occur during felt manufacturing processes especially if ventilation is poor. The major hazards associated with felts application are skin burns and adverse effects from fume exposure; the highest exposure takes place when heating/handling the hot (>200°C) mopping bitumen.

Liquid roofing products are manufactured, handled and layed at moderate or ambient temperatures. The health hazards in these situations are associated with the use of solvents with most formulations.

5.4.5. Industrial Applications

Industrial applications are varied and cannot therefore be covered by general statements. The health hazards will depend upon the procedures involved, e.g.

- Lining and waterproofing operations may be considered as roofing or paving, depending upon the technique.

- Flooring requires handling of hot mastic asphalts that are often laid by hand in enclosed areas. The hazards are of the same type as those encountered in using hot bitumen mixes, but the potential exposure to fumes is higher because of the use of much higher temperatures (around 250°C), sometimes with reduced ventilation. The bitumens are usually hard grades.

- Protective coating may give rise to concern when applied diluted in a solvent which often contains aromatic hydrocarbons.

- Paper or cardboard impregnation is carried out a moderate temperature and the end product is usually applied at ambient temperature.

6. EXPOSURE LIMITS

Some countries have specified limits for bitumen fume exposure, whereas other specify limits for benzo(a)pyrene or total PAC that are present in fume, see **Table 6.**

Table 6: Limits specified for bitumen exposure in a number of countries

United States of America	The American Conference of Governmental Industrial Hygienists (ACGIH) has recommended an 8 hour time weighted average Threshold Limit Value (TLV-TWA) of 5 mg/m^3 for Asphalt (petroleum) fumes. No short-term exposure limit (TLV-STEL) is proposed.
United Kingdom	The Health and Safety Exectuive recommend an 8 hour time weighted Occupational Exposure Standard of 5 mg/m^3 for Asphalt, petroleum fumes. They also recommend a 10 minute Short-term exposure limit of 10 mg/m^3.
The Netherlands	A standard of 5 mg/m^3 is advised for Asphalt (petroleum fume).
Germany	Bitumen is classified as being justifiably suspected of having carcinogenic potential. In view of this classification there is a requirement to control exposure as much as possible.
France	No limit quoted for bitumen.
Finland	No limit quoted for bitumen.
Norway	No limit quoted for bitumen.
CIS	No limit quoted for bitumen.
Sweden	No limit quoted for bitumen.
Denmark	A standard of 5 mg/m^3 is advised for bitumen fume.
Belgium	Adopts ACGIH values.
Italy	Uses ACGIH values.

7. HANDLING ADVICE

The primary hazards to be addressed is assessing the risks to health when working with bitumen are skin contact with the material, including contact via condensation of fume on the skin or on process equipment and inhalation of fumes. This focuses attention on the two very important aspects of prevention of adverse health effects:

- Personal hygiene and the use of protective equipment to minimize skin exposure.

- Maintaining temperatures at as low a level as practicable to minimize fume generation.

7.1. PRECAUTIONS

7.1.1. Personal Protective Equipment

Bitumen is commonly handled as a liquid at temperatures above 100°C and protective clothing is necessary to prevent burns by skin or eye contact.

Personal protective equipment should be selected to suit the operations in question, but where hot bitumen is being transported or used, it should include:

- Overalls with close-fitting cuffs and leg-ends designed to shed splashes away from the body.

- Face and eye shields.

- Heat resistant gloves.

- Heat resistant heavy duty boots.

If splashing is likely then additional requirements are:

- Full head and face protection.

- Neck cloth.

Where hot bitumen is handled in confined spaces, half-face respirators should be used and effective local artificial ventilation provided if possible.

In situations where bitumen is encountered in the form of an aerosol, mist or fume, e.g. around spraying operations, it is also necessary to avoid skin contact by the use of protective equipment such as overalls, gloves and boots. Further measures may be necessary, such as the use of respiratory protective equipment, when handling or applying cutbacks containing organic solvents or bitumen derivatives. Advice should be sought from the suppliers' safety data sheets.

7.1.2. Plant/Process Design

Designers of application equipment for bitumen should take the opportunity to create an environment which:

- Reduces the potential for excessive fume generation, e.g. by effective temperature control of roofing kettles and other heating equipment.

and/or

- Isolates the worker from the area of fume generation, e.g. by providing a protective ventilated enclosure for the spray-bar operator and aggregate distributor in surface dressing applications.

Where fume emissions from bitumen handling and loading operations create an environmental nuisance some form of vapour recovery system, vented to atmosphere via filters, can be considered.

7.1.3. Working Procedures

Control must be exercised over operating temperatures in order to maintain fume emissions at a low level. Bitumen should be stored and handled at the lowest temperature commensurate with efficient use. This is important in all cases, e.g.:

- Transfer operations of hot bitumen
- Road making operations by hot mix or spray applications
- Use of melting kettles for roofing applications
- Use of hot '*mastic*' asphalts, e.g. in hand-laid flooring applications

In the special case of recycling of old asphalt pavements, consideration must be given to the possibility that the old asphalt layer may contain components such as coal tar products, which have significantly higher PAC content than bitumen. Greater care must be taken to avoid exposure to the fume hazard in this case, especially if a hot recycling process is to be used.

Another situation where the potential for exposure is higher is during maintenance work on equipment, tanks etc. This will require the preparation of defined systems of work incorporating the use of personal protective equipment and possibly respiratory protection. Depending on the circumstances it may be necessary to install local exhaust ventilation at the point of fume generation or provide some dilution ventilation to the worksite.

7.1.4. Personal Hygiene

Adoption of a very high standard of personal hygiene is essential in any operation where there is a risk of skin contact with bitumen products and/or condensed fume. Washing facilities with a non-solvent based skin cleaner, hot water and soap should be provided and used. It may be necessary to provide skin conditioning cream if contamination and washing is frequent.

Overalls should be changed frequently and dry cleaned. Grossly contaminated clothing should be changed immediately and contaminated rags should not be kept in overall pockets. The condition of gloves should be checked before use for signs of wear and internal contamination, and discarded if necessary.

7.1.5. Monitoring

Regular monitoring of work practices and hygiene procedures should be carried out, as well as checks on the condition of protective equipment.

Whilst not being a control measure the importance of monitoring the environment, both by air sampling and observation, should not be underestimated. This provides the method by which it may be confirmed that control techniques are having the required effect.

8. EMERGENCY TREATMENT

Emergency treatment of persons exposed to bitumens and bitumen derivatives requires judgement depending on the circumstances of each case. Therefore, whenever possible, first-aid treatment should be carried out or supervised by appropriately qualified persons.

8.1. INHALATION

The following remarks apply to any situation where a person is overcome by noxious fumes even though such a result is considered improbable as a consequence of exposure to bitumens. In such an unlikely event, the normal practices should be followed for removing casualties to fresh air from the contaminated atmosphere or enclosed space; these include the use of breathing apparatus and paying special attention to the possible presence of hydrogen sulphide. Respiration and pulse of the casualty should be monitored and oxygen may be given if available. Respiration should be assisted if necessary using exhaled air resuscitation or a resuscitator if available. External cardiac massage should be given if necessary. The casualty should be kept in the recovery position and medical assistance obtained

8.2. INGESTION

In the unlikely event of ingestion of bitumen and bitumen derivatives do not give anything by mouth and ***do not*** induce vomiting. (Note: Spontaneous vomiting is a likely consequence of ingestion and if a cutback bitumen or emulsion is involved there is the associated risk of aspiration. If vomiting occurs, try to protect the airway.)

8.3. ASPIRATION

If there is any suspicion that aspiration of a cutback or emulsion into the lungs has occurred, obtain medical assistance immediately. Observe breathing and assist if necessary. Give oxygen if available.

8.4. SKIN CONTACT

In the event of accidental skin contact with hot bitumen, no attempt must be made to remove the bitumen from the skin. The injured part should be plunged into or under cold running water immediately for up to 10 minutes. In the case of a circumferential burn with adhesion of the bitumen, the adhering material should be split to prevent a tourniquet effect as it cools. Contaminated clothing may be removed provided it is not adhering to the skin. Obtain medical assistance immediately.

8.5. EYE CONTACT

If hot bitumen is splashed into the eye it should be cooled immediately under cold running water for at least 15 minutes. Medical attention must be obtained.

In the event of eye contact with cold bitumen, immediately flush gently with copious amounts of cold water. if irritation persists, obtain medical advice; if there is bitumen in the eye it may be advisable to refer the patient to an eye specialist.

8.6. INFORMATION FOR DOCTORS

No attempt should be made to remove firmly adherent bitumen from the skin!

Once it has cooled, bitumen is not harmful and in fact provides a sterile cover over the burnt area. As healing takes place; the bitumen will detach itself, usually after a few days.

If, because of the site of contact it becomes necessary to remove the bitumen, liberal amounts of warm medicinal paraffin can be used. Alternatively, a blend of medicinal paraffin and kerosine may be used; care should be exercised however since kerosine may cause skin irritation. After any solvent treatment the skin should be washed carefully with soap and water followed by the application of a proprietary defatting agent or skin cleansing cream. Only medically approved solvents should be used to remove bitumen from burns as other solvents could cause further skin damage.

9. DISPOSAL

Land filling with *Reclaimed Asphalt Pavement* (RAP) and spill of bitumen has been a common method of disposal for waste bitumen products. The risk for leakage to ground water from this product group is negligible due to the low water solubility.

RAP can be recycled with either cold or hot technique. However precautions must be taken if the RAP contains harmful non-bituminous products.

Wastes of bitumen derivatives which Eire easy to pour and handle at ambient temperature should be regarded as hazardous wastes. Accidental spillage may damage ground water. Disposal of these materials can best be achieved by burning in a special boiler facility.

Bitumen emulsions should be disposed of in the same manner as the unemulsified binder itself.

10. FIRE AND EXPLOSION HAZARDS

For details of recommended practices In prevention and treatment of fire and explosion hazards for bitumen, guides or codes such as those produced by the American Petroleum institute or the UK Institute of Petroleum should be consulted.

10.1. FIRE PREVENTION

Apart from cutbacks which have flash points associated with the diluent, bitumens and bitumen derivatives have flash points well above 150°C. However, because storage and handling is usually at high temperatures, precautions are necessary to prevent fires and explosions. For example, the vapour space in heated storage tanks must be controlled to keep evolved vapours outside the flammable range by ventilation or regulation of the storage temperature, or the vapour space must be blanketed with inert gas. Precautions against sources of ignition must be observed.

Modified Bitumens may, when overheated produce decomposition products having a lower flash point than the parent material.

10.2. CONTAMINATION BY WATER

Contamination of bitumen products by water should be avoided, as it results in violent foaming when the temperature is raised above 100°C and may cause the bitumen to overflow.

Hot bitumen must never be filled into a tank or other container without first checking that the container is completely dry. Contact of hot bitumen with water leads to violent expansion as the water turns to steam, and this can give rise to dangerous boil over and may cause damage to, or complete loss of, the tank roof.

11. ENVIRONMENTAL HAZARDS

No data have been located directly bearing on the ecotoxicology of bitumens. [57] However, an appraisal can be made based on the physicochemical properties of the constituents of bitumen.

Bitumen contains hydrocarbon compounds in the molecular weight range from 500 to 15 000. Water solubility will be so low that significant migration of the material into water is improbable. Concentrations acutely toxic to aquatic organisms will not occur and significant bioaccumulation is unlikely because of the high molecular weight of the hydrocarbons. [58]

In view of their low bioavailability, the components of bitumen are not biodegraded to any significant extent in the environment.

Hazards associated with bitumen derivatives must be treated on a case by case basis.

11.1. EMISSIONS

Processes which involve the use of bitumen-containing materials at elevated temperatures release fumes. Therefore, an important way of reducing emissions is to keep the bitumen temperature as low as possible.

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APPENDIX I BITUMEN ENTRIES IN EINECS

Bitumens (asphalts) and vacuum residues

232-490-9 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 C_{25} 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 seperation as the raffinate from a residual oil in a deasphalting or decarbonization process.

265-057-8 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 C_{34} and boiling above approximately 495°C (923°F)

265-188-0 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 sulfur compounds. It consists of hydrocarbons having carbon numbers predominantly greater than C_{34} and boiling approximately above 495°C (923°F)

265-196-4 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.

295-284-8 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.

295-518-9 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 C_{34} and boiling above approximately 495°C (923°F).

302-656-6 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 C_{80} and boiling above approximately 450°C (842°F).

309-712-9 100684-39-7

Residues (petroleum), distn. residue hydragenation

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 C_{50} and boiling in the range above approximately 360°C (680°F).

309-713-4 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 C_{50} and boiling in the range above approximately 500°C (932°F).

APPENDIX II

Bitumen derivatives, their manufacture and use

II.1 Bitumen Derivatives

- ***Cutback Bitumens***
  are mixtures of bitumens with volatile petroleum diluents such as white spirit, kerosine, or gas oil to render them more fluid for ease of handling and application. Depending on the level and volatility of the diluent used, the original properties of the bitumen may be partly or completely recovered by evaporation after application of the cutback. Cutbacks are sometimes heated for handling and application to temperatures up to 175°C. Grades are designated either by the temperature required to achieve a specified viscosity or by the viscosity at a specified temperature. Cutback grades are mainly used in road surface dressing.

- ***Fluxed Bitumens***
  are mixtures of bitumens with fluxes (high boiling petroleum products such as industrial process oils, or heavy distillates typically with initial boiling points above 350°C) to make products which are easier to use in certain applications. There is only limited evaporation of the flux after applications. Grades are designated by their viscosity. There are a limited number of applications, mainly in the Nordic countries.

- ***Bitumen Emulsions***
  are fine dispersions of bitumen in water, where bitumen is the dispersed phase, and water is the continuous phase. They are normally manufactured from penetration grades using a high shear milling system; other special equipment may be used for some industrial emulsions. Some emulsions may contain fluxing agents and/or volatile diluenls either added during production or previously blended. The *"bitumen solids"* content of an emulsion varies between 40 and 80 per cent and application temperatures range from ambient to 90°C. Normally higher solids content emulsions require higher application temperatures. Three types exist according to the type of electrical charge imparted by the stabilising agent (emulsifier or soap solution) to the bitumen particles; anionic, cationic and nonionic. Cationic emulsions are used most frequently, and in many parts of the world they are more widely used than cutback bitumens. Some special emulsions may be manufactured from modified bitumens, or have polymers added in the form of a latex.

- ***Modified Bitumens***
  are bitumens in which the rheological properties have been substantially changed by the addition of a physical or chemical agent. This would normally be an elastomeric or plastomeric agent (Polymer Modified Bitumen or PMB). They are mainly used in road construction, roofing and waterproofing, sometimes at elevated temperatures (up to 230°C). No formal classification system is in common use, however in Germany a classification system for road construction does exist and a system is being prepared by a CEN working group.

II.2 Manufacturing Processes

Distillation

Normally this takes place in two stages: atmospheric distillation at normal pressure and vacuum distillation under reduced pressure.

In atmospheric distillation, crude oil, after desalting, is heated to a temperature usually ***not*** exceeding 385°C and introduced into a fractionating column. Volatile fractions such as gasoline, kerosine and gas oil components, are separated and drawn off at selected levels of the column. The heavier hydrocarbons, known as the atmospheric residue and having the consistency of fuel oil, are removed at the bottom of the column.

This atmospheric residue is normally fed, at a temperature up to approximately 380°C, into a second fractionating column. Pressure is reduced to a very low level to permit distillation at lower temperatures and avoid undesirable thermal cracking. Lubricating oil distillate fractions are separated and drawn off. A vacuum residue is removed from the bottom of the column.

With heavy bituminous crudes, the vacuum residue is often a "*commercial*" bitumen. With lighter crudes it is a feedstock for further processing.

Air Blowing

This refining process consists of introducing air under pressure into a bitumen feedstock usually heated to between 220 and 300°C in a reactor. Both continuous and batch processing are used, sometimes in the presence of a catalyst. Oxidation and condensation reactions occur resulting in formation of higher molecular weight compounds which give a harder and less temperature susceptible bitumen. Moderate blowing is used to obtain hard road bitumens whilst severe treatment produces oxidized bitumens suitable for a wide range of building and industrial applications.

Thermal Conversion

This process results in the reduction of large paraffinic molecules to smaller ones. To a lesser degree a condensation occurs increasing asphaltenes and resin. Thus the process may be utilized to modify the ratio between paraffins, resins and asphaltenes using residues from lighter crudes than conventional ones. Temperatures up to 450°C are used but at a pressure of 15 to 20 atmospheres. During the cracking process some PAC generation occurs, and the thermal residue obtained is then distilled in a vacuum unit, to remove volatiles including the PACs, and the residue of this subsequent distillation can then be used as a component for bitumen.

Solvent Precipitation or Deasphalting

Many vacuum residues are the source of valuable high viscosity base oils for lubricants generally known as bright stocks. Part of the process of refining bright stocks is the removal of asphaltic compounds by solvent treatment. Liquid propane or propane/butane mixture is generally used (at around 60°C and under sufficient pressure to maintain it as liquid) to dissolve the oil. The asphaltic fraction is precipitated and drawn off from the bottom of the tower and may be used in the manufacture of bitumens.

Blending

Components are blended to achieve required specifications, for example the blending of two distillation residues of different penetration levels. Blending may be of the batch type in storage tanks with mixing facilities or continuous in-line blenders which ensure homogeneous mixing of two or even three components with a high degree of precision

Ancillary Processess

Additional blending and fluxing processes may be used to provide further flexibility by use of fluxes and/or additives to manufacture bitumen derivatives. Auxiliary processing may also include the manufacture of bitumen emulsions.

II.3 Composition

Conventional chemical analysis shows that bitumens contain mainly carbon and hydrogen with small amounts of oxygen, nitrogen and sulphur and trace amounts of metals. A typical analysis is 83% carbon, 10% hydrogen, 7% oxygen, nitrogen and sulphur and trace amounts of vanadium, nickel, aluminium and silicon.

More complex methods of analysis, for example, infrared, ultraviolet and nuclear magnetic resonance, identify classical chemical groupings and confirm that bitumens are complex mixtures, mainly of high molecular weight hydrocarbons.

Using a selective solvent such as normal heptane, bitumen may be separated into asphaltenes (which are precipitated) and an oily fraction (maltenes). With adsorption chromatography the maltene fraction may be separated further into resins, aromatic oils and saturated oils. These four groups of constituents differ in nature:

- ***Asphaltenes***
  are brittle brown to black amorphous solids. They contain mainly carbon and hydrogen but also oxygen, nitrogen and sulphur. Chemically, they consist of highly condensed aromatic compounds of high molecular weight. The concentration of asphaltenes varies with a higher proportion in the harder bitumens.
- ***Resins***
  are brown to black, adhesive, shiny solids or semi-solids. They contain mainly carbon and hydrogen but also small amounts of oxygen, nitrogen and sulphur. Chemically they stand between the asphaltenes and the aromatics.
- ***Aromatic Oils***
  are viscous dark brown liquids comprising mainly carbon, hydrogen and sulphur with minor amounts of oxygen and nitrogen. They contain numerous naphthenic-aromatic ring compounds
- ***Saturated Oils***
  are viscous liquids or solids which range from straw to white colour. They consist mainly of long chain saturated hydrocarbons with some branched chain compounds, alkyl aromatics with long side chains, and cyclic paraffins (naphthenes).

Average molecular weights cover a continuous range from saturated and aromatic oils (500 to 1000) through resins (1000 to 2000) to asphaltenes (greater than 2000).

Bitumens have a colloidal nature in which large structures (the asphaltenes) are dispersed in the form of micelles in an oily liquid phase (the maltenes). Depending on the relative proportions of the four groups described above the structure will vary between "*sol*" in which the micelles are dispersed and a "*gel*" in which micelles are organized to more network-type structures. Thus, saturated oils which have little solvency power for asphaltenes, promote a predominantly gel character; aromatic oils have greater solvency power and promote a predominantly sol structure.

Composition, structure and behaviour are related. For example, air blowing changes aromatic oils to resins and resins to asphaltenes. Heavily blown bitumens have a predominantly gel character which has reduced temperature susceptibility. Deeper distillation will preferentially reduce the saturated oil content and give a bitumen which is more sol in character and has greater temperature susceptibility. Thus, an understanding of composition and structure assists in interpreting the rheological behaviour of bitumen and the effects of changes in temperature.

Polycylic Aromatic Hydrocarbon (PAN') Content of Bitumen and its Fumes

Although PAHs exist in crude oils, [59] they are generally present in more limited amounts in bitumens. [2,3] This is because the principal refinery processes used for the manufacture of bitumens, contain a vacuum distillation step which materials with low to moderately high molecular weight, including most PAHs with 3-7 fused rings. The temperatures involved in the vacuum distillation process are not high enough to result in any substantial PAH generation.

The levels of PAH found in penetration and oxidized bitumens are shown in **Table 1** together with the sources of the data. One of the penetration grades analysed by [2] was excluded from the table as its PAH levels were in the order of 10x greater than the rest (interestingly this sample did not have clearly greater biological activity (**see Section 4.3.1**). The other bitumens of penetration or oxidized grades had only low bevels of PAHs. Compared with coal tar pitch, PAH levels in bitumen ranged from 4-5 orders of magnitude less (10^4-10^5). [3]

When bitumen is heated to allow application, fumes are given off and these have been condensed and analysed. Invariably the PAH content of the condensed fume is greater than that of the parent bitumen (see **Table 1**). **<u>NO</u>** substantial differences exist between the PAH contents of condensed fumes generated from penetration or oxidized bitumens heated to similar temperatures. The temperature of fume generation affects both the relative proportions of individual PAHs in the fume and amounts of fume generation. Comparing the condensed fumes obtained from generation temperatures of 160°C and 250°C (**Table 1**) the lower temperature fume contained higher levels of 3-4 ring PANS whereas the higher temperature fume contained slightly greater levels of 5+ ring PAHs.

At higher temperatures (316°C) the situation becomes more confused probably because non-PAH components increased in amount. Hence no clear conclusions can be reached on the relative concentration of carcinogenic PAHs in the condensed fumes from different generation temperatures. However the amounts of fumes generated at different temperatures are much more relevant to human PAH exposure. It has been reported that eighty-fold more fume is given off at 250°C than at 160°C, hence temperature control will considerably reduce emissions of PAHs from bitumens. In comparison, the condensed fumes from heated coal-tar pitch contain approximately 500 times more PAHs than condensed bitumen fumes and emission levels of PAHs from heated coal-tar pitch are approximately three or four orders of magnitude greater. [3]

II.4 Major Applications

Road Paving

i) Hot-Mixes

Bitumen is added to hot aggregate, either in a batch operations, or continuous process. Normally penetration grades are used, although hard grades, cutbacks, emulsions and modified bitumens are used to provide specialist products.

ii) Surface Dressing

One or more bitumen layers are sprayed onto a road surface, and immediately covered by aggregate. Cutback bitumen or emulsion would normally be used but in special circumstances modified bitumens or penetration grades may also be used.

Note: ***Recycling***
In its broader concept pavement recycling covers the re-utiliation of road-making materials, by recovery from the existing rod pavement. It may be subdivided ino various methods as defined below:

Hot in-situ:
The removal or partial removal of the existing asphalt layer either by milling or hot scarifying, and the in-situ re-application of these materials . This process may include heating of the reclaimed asphalt pavement (RAP) and the addition of virgin materials.

Hot in-plant:
The asphalt layer removed either by cold milling or in partial block form, is then transferred to an asphalt plant where the material is crushed and graded (if required) and then added to virgin material in an asphalt mixing plant. The ratio of RAP to virgin materials depends largely on the design of the asphalt plant, and the heat transfer mechanism used to heat the RAP.

Cold in-plant:
As above but using bitumen emulsions, and not heating stage.

Cold in-situ:
The total or partial removal of an asphalt layer, and/or base material either by milling or scarifying followed by a further material classification stage if appropriate, after which the resulting material is mixed with bitumen emulsion and recompacted.

Roofing

In Europe, the major outlets for bitumens in roofing are the manufacturing of rolled bituminous membranes and as a mopping adhesive for the former. Some bitumen is being used in liquid roofing formulations. The manufacturing of bitumen shingles is a limited application. Roofing membranes manufacture involves either a plain blown bitumen or a penetration grade bitumen modified with polymeric materials.

The use of the latter requires a blending step, where the bitumen is heated up to 160-200°C and modified with polymers. The membrane coating medium may contain a mineral charge at the same temperature range as above; the coating mixture is then applied to a reinforcing matting and formed as a surfaced roll. Rolls are installed on the roof either by welding with a flame, taking advantage of a controlled melting of the bottom of the membrane, or by use of a hot "*mopping*" bitumen adhesive; fumes evolution may be observed during those operations.

Mopping bitumen is a blown grade with a high Ring and Ball Softening Point; it is heated to a high temperature in kettles (up to 200-250°C) and spread onto the roof with brushes.

"Liquid roofing" materials are fluid pastes containing bitumen, various additives and inorganic materials and solvents. They are cold-applied and therefore do not generate bitumen fumes in normal use.

Other applications

The following is a list of applications and is not exhaustive:

- lining of canals, water reservoirs, dams and dikes;
- flooring;
- mastic application;
- protective coating for walls, pipes, water mains, motor cars;
- paper or cardboard impregnation;
- components of products such as adhesives. joint fillers, paints, lubricants, rubbers, etc.;
- coal briquetting;
- electrical insulation;
- manufacture of electric batteries;
- encapsulation of radioactive materials;