

OIL CONTAMINATED WASTES – SWAN04 – ERRATUM 04 MAY 2007

Please note that the sentence “A hydrocarbon is not carcinogenic if it contains less than 0.0005% w/w (50 mg/kg) of this PAH” found in the middle of paragraph 7, page 2 of SWAN04 should read “A hydrocarbon is not carcinogenic if it contains less than **0.005%w/w** (50 mg/kg) of this PAH”

SPECIAL WASTE REGULATIONS 1996 SPECIAL WASTE ADVISORY NOTE

OIL CONTAMINATED WASTES

Ref: SWAN/04

Background

Oil contaminated waste can arise in industrial production processes, end of life products, clean up operations and waste treatment. The EWC has many references to wastes containing oil, but oil may be a dangerous substance in other wastes. In judging whether the waste is special, information may be at hand such as analyses or the data suppliers require for safe handling of material. However waste holders may not always be familiar with the composition of the waste.

Oils can be a complex mix of hydrocarbons, and analysis should be chosen to reflect likely contaminants. Many are classified as single substances on the ASL¹ and should be treated carcinogenic. A generic threshold of 0.1% in the waste can be based on a conservative assumption of worst case carcinogens: Assessment does therefore not necessarily depend on identification of individual hydrocarbons.

Where the oil is unknown or a complex mixture or some substances cannot be classified, it is possible to identify whether the oil itself is hazardous by 'marking' for a known carcinogen. **A negative test against a threshold or a marker will not disqualify that other hazards, such as flammability or those from other contaminants may be present.** If analysis or marker tests are difficult to do, the only resolution may be to test for a hazardous property directly (see Appendix C of WM2).

This note gives general information on the nature of different types of oil in a waste that will help in determining whether it is special (hazardous).

Waste Assessment

Hydrocarbon fractions

Oils are usually **petroleum** based substances, although some are coal derived. The hydrocarbons are made up of chains of different lengths. Those with a ring structure (e.g. BTEX, PAHs) are 'aromatic' and those with an open chain structure (e.g. alkanes) are 'aliphatic'. The shortest chain hydrocarbons are gases, longer ones are liquids and get more viscous or 'heavier' as chain length increases. The longest chains are solids like fats, waxes and greases. Lighter fractions tend to be used as solvents or in dry cleaning and quick drying/degreasing agents and may also be blended for use in **petrol** (gasoline).

Diesel is similar to petrol as an aliphatic product of crude oil distillation, and is used in heating oil. Kerosene ('paraffin oil') is used in lighting or jet fuel. Heavier fuel oils may be used in ship engines. Generally, C₅ – C₁₂ applies to 'petrol range' organics, and C₁₀ – C₃₀ or higher to 'diesel range' organics. There are several definitions of 'mineral oil' but it generally lies within the range C₅ – C₂₅. A lubricating mineral oil will typically fall in the C₁₆ - C₂₅ range. However, these are generalisations since the ASL lists diesel and gas (fuel) oils up to C₂₆ and lubricating oils up to C₅₀.

Refined mineral oils are used in insulating (transformer) oils and may contain polychlorinated biphenyls.

Chains above about C₂₀ form solids, starting with paraffin wax. **Bitumen**, also known as 'asphalt tar' or pitch, is a black, viscous liquid produced from fractional distillation of crude oil (unrefined petroleum). It is supplied by the oil industry for use in roofing materials or as a binder to aggregates in roadstone coating. It is blended from various components (e.g. plasticisers) to meet specification, e.g. flux oil or diesel may be added to soften the mix. Some bituminous mixtures are semi-solid, for instance **asphalt concrete**.

The term tarmac(-adam) is a trademark describing the tar like appearance of bitumen. This should not be confused with natural or coal tar which was phased out in the 1960s in road building. **Coal tar** is the liquid by-product of the distillation of coal to make **coke**, a light fuel used in the iron and steel industries.

Poly aromatic hydrocarbons (PAHs) are semi-volatile compounds derived from coal tar or present in distillation residues and used in the manufacture of plastics, dyes and solvents or in wood preservatives, insecticides and coating materials (e.g. anthracene). They are also formed by the incomplete combustion of petroleum substances or other organic constituents (e.g. in foundry sands). Their carcinogenicity generally increases with molecular weight or as water solubility or volatility decrease.

Assessment on total oil content and generic threshold

Oil products are classified in the ASL under generic names such as 'lubricating oil', 'kerosene', 'coal tar' and 'petroleum substances' (e.g. grease). These have the same status as a 'substance' and should be compared to the thresholds for hazardous (special) waste in WM2. It is not necessary to complete a full analysis to assess against each individual hydrocarbon. Heating and insulating oils are not on the ASL.

If it simply needs establishing that oil is or is not present to make the waste special, a generic threshold of **0.1%** is used. This is based on a worst case scenario of category 1 or 2 carcinogen substances (**H7**) (most of which are classified against Risk phrase R45²). This represents the first 'screen' and can be applied regardless of how complex the oil mixture is, but does not dispense the waste holder from investigating other potential hazards (e.g. from flammability **H3** or toxicity **H6**) or contaminants.

Assessment on individual hydrocarbons and 'marker' compounds

If the specific nature of the hydrocarbons making up the 'oil' content is known, or the source and type of contamination is understood the waste may be special against other thresholds. For instance diesel is a category 3 carcinogen (**H7**) and would make the waste special at 1%.

It should be noted that the carcinogenic (**H7**) property is assessed on whether an individual substance exceeds the threshold, other properties (e.g. **H14** eco-toxic) may be based on the concentration of substances being additive and exceeding the threshold.

If the analysis gives a range of hydrocarbons it is possible to assess whether the oil itself in the waste is carcinogenic. Some ASL listed oils are not carcinogenic if a 'marker' compound is present below a certain concentration. These markers can be used where (1) total oil is at the generic threshold of 0.1% but the producer wants to question whether the oil is carcinogenic or not; (2) where the nature of the oil is unknown and (3) where it might be mixed with other wastes such as a degreaser solvent.

The carcinogenicity of oil derived substances is usually associated with the PAHs, for which there are well established data. A common marker is **benzo-[a]-pyrene (B[a]P)**. A hydrocarbon is not carcinogenic if it contains less than 0.0005% w/w (50 mg/kg) of this PAH. Similarly, the classification as a carcinogen need not apply if the oil contains less than 0.1% w/w **benzene** or 0.1% w/w **1,3-butadiene**. The **DMSO** extraction test³ can also be used to indicate carcinogenicity from known petroleum-derived oils such as the heavier base oils and lubricants, where a higher limit of 3% in the oil applies.

The notes to the entry on the ASL should be checked as some substances are carcinogenic without qualification by a marker substance. Marker compounds apply to some 'petroleum products', coal tar, pitch, creosote, anthracene oils and paraffin oils or waxes.

The markers apply to the contaminating oil itself and not the waste as a whole. To be representative of the oil in the waste, they should be adjusted according to the total oil concentration. A total oil of 0.1% is a thousandth weight by weight of the waste, B[a]P would thus have to be present in the waste at a thousandth of 50 mg/kg, i.e. 0.05 mg/kg (or 1 mg/kg benzene and 30 mg/kg DMSO extract). There is no need to qualify whether oil is carcinogenic below a total oil concentration of 0.1% (the generic threshold).

Since markers may be listed themselves as entries in the ASL, they would not be used alone in comparing to the special waste threshold where it was already known the total oil content exceeded it. Where the same substance is entered with more than 1 marker compound, the test should be based on the marker with the lowest limit. The waste must still be assessed against all of the appropriate hazards.

If the holder cannot decide which substances might be present, he would simply use the generic threshold above. If a carcinogenic test is required, B[a]P for the unspicated total (TPH etc.) should be used unless there may be justification for another marker, e.g. the oil is likely to be depleted in PAHs.

The waste holder must make their own judgement on a definitive approach to classification of their waste and balance the costs of providing this information to support a contention that the waste is or is not special.

Assessment where data gives non-ASL classified substances

The Special Waste Regulations take as their primary source of data the classifications of substances on the ASL. However a substance may not be listed on the ASL. Where it is listed, the determination of special waste may not be consistent with hazard assessment under CHIP. CHIP uses the ASL to identify the hazards of chemicals for supply and gives guidance on the use of R phrases. Mixtures requiring labelling under CHIP may therefore not always be special waste, and material safety data sheets should only be used where the oil has not been put to use or undergone any changes in composition. Final mixtures not covered by CHIP would include used 'engine', 'heating' or 'quenching' oil.

The COSHH Regulations list some carcinogens not included on the ASL (e.g. used engine oil), or included but not classified carcinogenic. **The assessment of special waste would only consider such sources where the ASL gave no entry.**

Analytical techniques

Knowing the likely nature of hydrocarbons will help the scope of the desktop assessment and the type of analysis if this is required. It will also aid use of an appropriate 'marker' as given above. Total oil content such as **TPH** (Total Petroleum Hydrocarbons) or **TEM** (Toluene Extractable Matter) will be sufficient where the nature of the oil contamination is not well understood as they are general screens for organic compounds. However, it is common for speciation of hydrocarbons to be given.

SEPA cannot sanction the use of any technique as the waste producer or holder should establish which is appropriate based on sound reasoning and evidence. However general guidelines may help ascertain whether adequate analytical steps are taken in determining the status of oil contaminated wastes.

TEM pulls out a wide range of organics from C₅ to C₄₀, and **pet ether** even heavier fractions. It should be noted that some solvent based extractants such as toluene may also strip out natural organic matter. A physical description of the extract may help (e.g. is it glossy or tar-like or a liquid). A more definitive interpretation of fractions may be made by gas chromatographic (GCMS) or infra red (e.g. FT-IR) scan on the extract. With GCMS this would be on the basis of individual compounds, with IR it might be related to the relative proportions of aliphatic and aromatics in the sample as a whole.

PAH's can be identified by extraction followed by GCMS or High Performance Liquid Chromatography (HPLC) with UV and Fluorescence detectors. SEPA can perform HPLC.

The closest current method to the determination of oil content in SEPA's laboratories is FT-IR. SW area carry out GCMS screens and tentatively identify individual compounds: For oil type analysis using GCMS the fingerprint obtained can be interpreted. The methods currently in use for quantitative analysis of PAH components are for water and sediment, the laboratory does not have a method for dealing with solid or liquid waste and the methods for water and sediment may not be transferable.

TPH analysis should cover an adequate range of carbon chain lengths to include the expected forms of oil present in the waste. Where the nature of the oil is unknown it is important that the TPH analysis includes petrol range organics, diesel range organics and mineral oil range organics, ideally covering the range of carbon chain lengths from **5 to 35**.

Waste Classification

Oil contaminated wastes where there is no specific reference to oils in the EWC

Oil contaminated wastes may be caught by entries in the EWC without a specific reference to the hydrocarbon as a dangerous substance. Examples are lubricating greases and solvents for degreasing car parts, classified as **11 01 13*** (B32, WM2) and excavated contaminated soils or mixed construction and demolition wastes, **17 05 03*** and **17 09 03*** respectively. Petroleum products and chemicals are also used in the manufacture of detergents, artificial fibres, plastics, insecticides, fertilisers, pharmaceutical preparations, toiletries, and synthetic rubber. The oil in the waste is assessed in relation to the threshold levels in the same way as if there was a specific reference to it.

Street sweepings and other similar 'municipal' wastes are classified non-hazardous under Chapter 20. Other gully emptyings or oily waters from industrial interceptors, vehicle repair shops etc. would be classified under Chapter 13 or **16 10 01*** (aqueous liquid wastes containing dangerous substances) if they required off site treatment.

Oil contaminated wastes where there is specific reference to oils in the EWC

Type of oil containing waste	EWC entry (& non-hazardous mirror)	WM2 ref.
Drilling muds	01 05 05* (01 05 07 / 08) (see below)	B3/4
Wastes from petroleum refinery	Chapter 5	B9-11
Oil fly ash from incinerators	10 01 04*	B24
Water cooling treatment	Chapter 10	B24-26
Tar wastes from electronics industry	10 08 12* (10 08 13)	B26
Machining oils	Chapter 12 01	B34
Grinding etc sludges	12 01 18* (12 01 99)	B34
Oil interceptor waste	Chapter 13 05	B36
Industrial gulley waste emptyings	Chapter 13 05	B36
Oily wipes and granules/clean ups	15 02 02* (15 02 03)	B40
Oil filters from metal fabrication	15 02 02* (15 02 03)	B40
Oil filters from vehicles	16 01 07*	B43
Transport/storage tank cleaning	16 07 08* (16 07 99)	B46
Bitumen roofing felt	17 03 01* (17 03 02)	B46
Cables from construction/demolition	17 04 10* (17 04 11)	B49
Road surfacing wastes	See below	B49
Waste treatment wastes	19 02 07*	B54
Water treatment works waste	19 08 10*	B55

There may be additives or contaminants in oil containing wastes that confer hazardous properties other than carcinogenicity.

In their used forms, waste oils (hydraulic, insulating etc. oils, liquid fuels etc) are absolute entries in Chapters 12 and 13 in the EWC. B34-B37 in WM2 gives examples.

Drilling muds

Refined mineral oils tend to be used in modern drilling fluids, with the distillation process reducing the aromatic hydrocarbon content to about half that of diesel, which reduces toxicity. More recently synthesised hydrocarbons such as paraffins (alkanes) and olefins which have very low PAH content and offer more stability have also been used. Drilling fluids will be blended with other additives such as thinners, sodium hydroxide and lubricants to achieve the correct drilling performance.

Road surfacing wastes

Since modern road surfacing materials are bituminous mixtures, road planings or chippings would be classified non-hazardous by 17 03 02. There is no specific reference to bitumen as a dangerous substance but the ASL classifies 'pitch' as carcinogenic (R45²) and therefore it is advised that analysis or a marker test is carried out or a hazardous classification used: Bituminous mixtures containing coal tar are classified as a mirror entry 17 03 01*, but coal tar and tarred products themselves are absolute hazardous 17 03 03*.

Chapter 16 contains a mirror entry for organic substances containing dangerous substances 16 03 05*. This could be used to classify off-specification batches and unused products, such as road making material surplus to need.

Notes

¹ ASL (provides simple information for the labelling of products with chemicals that could be dangerous to human health or the environment) can be found online on the NCEC website at: <http://www.the-ncec.com/cselite/index.html> **WM2 uses the most recent version of the ASL to ensure that classification of waste reflects current understanding on dangerous substances**

² R45 – May cause cancer

³ DMSO (dimethyl sulfoxide) extraction test as measured by IP346. IP346 is a standardised method developed by the Institute of Petroleum and is globally accepted by legislators as a tool for classifying oils