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heavy fuel oils

Prepared by CONCAWE's Petroleum Products and Health Management Groups

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ABSTRACT

The dossier summarizes the physical and chemical properties and toxicological, health, safety and environmental information on heavy fuel oils.

KEYWORDS

Fuel oil, heavy fuel oil, toxicology, health, environment, review

CONTENTS

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 derivatives

- 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

Heavy fuel oils are blended products based on the residues from various refinery distillation and cracking processes. They are viscous liquids with a characteristic odour and require heating for storage and combustion. Heavy fuel oils are used in medium to large industrial plants, marine applications and power stations in combustion equipment such as boilers, furnaces and diesel engines.

Heavy fuel oil is a general term and other names commonly used to describe this range of products include: residual fuel oil, bunker fuel, bunker C, fuel oil No 6, industrial fuel oil, marine fuel oil and black oil. In addition, terms such as heavy fuel oil, medium fuel oil and light fuel oil are used to describe products for industrial applications to give a general indication of the viscosity and density of the product.

This dossier on heavy fuel oils collates the currently available data on all grades of heavy fuel oils and covers the health, safety and environmental properties of these products as sold for the industrial and marine markets.

2. DESCRIPTION

2.1. HEAVY FUEL OILS

Heavy fuel oil consists primarily of the residue from distillation or cracking units in the refinery. Historically, fuel oils were based on long residues (see section 2.2) from the atmospheric distillation column and were known as straight run fuels. However, the increasing demand for transportation fuels such as gasoline, kerosine and diesel has led to an increased value for the atmospheric residue as a feedstock for vacuum distillation and for cracking processes. As a consequence, most heavy fuel oils are currently based on short residues (see section 2.2) and residues from thermal and catalytic cracking operations. These fuels differ in character from straight run fuels in that the density and mean molecular weight are higher, as is the carbon/hydrogen ratio. The density of some heavy fuel oils can be above 1,000 kg/m^3, which has environmental implications in the event of a spillage into fresh water.

To produce fuels that can be conveniently handled and stored in industrial and marine installations, and to meet marketing specification limits, the high viscosity residue components are normally blended with gas oils or similar lower viscosity fractions (Kolpack, R.L. et al, 1978; Orr, A.S. and Van Sant Jr., R.W., 1960; Guard, H.E. and Cobet, A., 1972). In refineries with catalytic cracking units, catalytically cracked cycle oils are common fuel oil diluents. As a result, the composition of residual fuel oils can vary widely and will depend on the refinery configuration, the crude oils being processed and the overall refinery demand.

Residual fuel oils are complex mixtures of high molecular weight compounds having a typical boiling range from 350 to 650°C. They consist of aromatic, aliphatic and naphthenic hydrocarbons, typically having carbon numbers from C_{20} to C_{50}, together with asphaltenes and smaller amounts of heterocyclic compounds containing sulphur, nitrogen and oxygen. They have chemical characteristics similar to asphalt and hence, are considered to be stabilised suspensions of asphaltenes in an oily medium. Asphaltenes are highly polar aromatic compounds of very high molecular weight (2000-5000) and in the blending of heavy fuel oils, it is necessary to ensure that these compounds remain in suspension over the normal range of storage temperatures.

Heavy fuel oils also contain organo-metallic compounds from their presence in the original crude oils. The most important of these trace metals is vanadium. Some crude sources, for example, from the Caribbean area and Mexico are particularly high in vanadium and this is reflected in high vanadium contents in heavy fuel oils produced from these crudes. Vanadium is of major significance for fuels burned in both diesel engines and boilers because when combined with sodium (perhaps from seawater contamination) and other metallic compounds in critical proportions it can form high melting point ashes which are corrosive to engine exhaust valves, valve seats and superheater elements. Other elements that occur in heavy fuel oils include nickel, iron, potassium, sodium, aluminium and silicon. Aluminium and silicon are mainly derived from refinery catalyst fines.

Significant concentrations of hydrogen sulphide (H$_2$S) are known to accumulate in the headspaces of storage tanks that contain heavy fuel oils. Heating of such tanks may cause decomposition of some of the sulphur-containing compounds, which release H$_2$S. In addition to the hazard from H$_2$S, there is also evidence that

accumulations of vapours of light hydrocarbons are also to be found in the headspaces of heavy fuel oil tanks.

Appreciable concentrations of polycyclic aromatic compounds (PAC) can be present in heavy fuel oils depending on the nature and amount of the low viscosity diluent used and whether the residue component is cracked or un-cracked. If the residue components are from the atmospheric or vacuum distillation columns, the concentration of three to seven ring aromatic hydrocarbons is likely to be in the order of 6 to 8%; if heavy catalytically cracked or steam-cracked components are used, the level may approach 20% (CONCAWE, 1985). One of the diluent fractions commonly used is catalytically cracked cycle oil, which has been reported to contain 58% three to five ring aromatic hydrocarbons (Cruzan et al 1986)

2.2. HEAVY FUEL OIL BLENDING COMPONENTS.

Heavy fuel oils can be blended from a wide range of refinery components, the most important of which are:

Long residue: the residue from the atmospheric distillation of crude oil. As mentioned earlier, historically this was a major fuel oil blending component, but it is now mainly used as a feedstock for the vacuum distillation unit or for a thermal or catalytic cracking unit.

Short residue: the residue from the vacuum distillation of crude oil.

Thermal cracker or visbreaker residue: the residue from thermal cracking processes designed to increase the yield of distillate components from atmospheric and vacuum residues.

Cat cracker slurry oil (clarified oil): a heavy fraction from a catalytic cracking operation, a process for the conversion of heavy hydrocarbon fractions into high-quality gasoline components.

Thermally cracked or visbreaker gas oil: a middle distillate fraction from thermal cracker or visbreaker units.

Cat cracker cycle oil: a middle distillate fraction from the catalytic cracking unit.

Kerosine: a lighter middle distillate fraction from the atmospheric column.

Gas oil: a heavier middle distillate fraction from the atmospheric column.

Vacuum gas oil: a heavy gas oil fraction from the vacuum column.

The EINECS entries for heavy fuel oils and heavy fuel oil components are listed in **Appendix 1**.

3.   TYPICAL PROPERTIES

Marketing specifications have been established by a number of authorities to ensure the satisfactory operation of industrial and marine equipment utilising heavy fuel oils. Such specifications include ASTM D-396 (ASTM 1992), BS 2869 for inland fuels (BSI 1988), ISO 8217 for marine fuels (ISO 1996) and CIMAC requirements for residual fuels for diesel engines (CIMAC 1990).

Typical properties for heavy fuel oils can vary widely within the specification limits: normally they would be expected to fall within the ranges listed in **Table 1**.

Table 1:   Range of physico-chemical properties for heavy fuel oils

Property	Unit	Test method	Typical range
Kinematic viscosity at 100°C [1]	mm^2/s	ISO 3104	6.0 to 55.0
Density at 15°C	kg/m^3	ISO 3675 or ISO 12185	950 to 1010 [2]
Flash point	°C	ISO 2719	> 60
Pour point	°C	ISO 3016	< 30
Carbon residue	% (m/m)	ISO 10370	< 22 [2]
Ash	%(m/m)	ISO 6245	< 0.20
Water	% (v/v)	ISO 3733	< 1.0
Sulphur [3]	% (m/m)	ISO 8754	Inland < 3.5 Marine < 5.0
Vanadium	mg/kg	ISO 14597	< 600
Aluminium plus silicon	mg/kg	ISO 10478	< 80

Notes:

(1)   Throughout this dossier the SI units for kinematic viscosity, mm^2/s, are used, although in technical literature and specifications kinematic viscosity is often expressed in centistokes (cSt). (1 mm^2/s = 1 cSt)

(2)   ISO heavy fuel oil grades ISO-F-RML 45 and RML 55 have unrestricted density and carbon residue values.

(3)   It is proposed to reduce the sulphur content of certain liquid fuels (including heavy fuel oil). The purpose is to reduce SO_2 emissions from combustion. It is proposed to restrict as from the year 2005 the sulphur content of these fuels to <1%.

4. TOXICITY

4.1. PRODUCTS STUDIED

The toxicity of a heavy fuel oil depends on the toxicity of the individual stocks from which it is blended. API, CONCAWE, and others have investigated the toxicity of a number of heavy fuel oil components. Heavy fuel oils are generally minimally irritating to the eye and skin and are not appreciably toxic after a single oral or dermal exposure. Repeated dermal exposure may cause significant toxicity or dermal carcinogenicity. When cracked stocks and high-boiling distillates are present, the fuels may be systemically toxic as well as dermally carcinogenic.

A list of heavy fuel oils and components for which toxicity data are available is given in **Table 2**.

Table 2: Heavy fuel oils and components for which toxicity data are available

Material	CAS No.	Source
No. 6 Heavy fuel oil	68553-00-4	API, Sample 78-6
No. 6 Heavy fuel oil	68553-00-4	API, Sample 78-7
No. 6 Heavy fuel oil	68553-00-4	API, Sample 78-8
No. 6 Heavy fuel oil	68553-00-4	API, Sample 78-9
Catalytically cracked clarified oil	64741-62-4	API, Sample 81-15
Steam-cracked residue	64741-62-4	DSM
Clarified slurry oil	64741-62-4	Feuston et al, 1994
Heavy coker gas oil	64741-81-7	Feuston et al, 1994
Syntower bottoms	64741-62-4	Feuston et al, 1994
Visbreaker gas oil	64741-81-7	Feuston et al, 1994
Steam-cracked tar	64742-90-1	Smith et al, 1951

4.2. ACUTE TOXICITY

4.2.1. Oral and skin

Acute systemic toxicity data (oral and dermal) for a number of heavy fuel oil components and blended fuels are summarized in **Table 3**.

Table 3: Summary of acute systemic toxicity data for heavy fuel oils

Material	Oral LD_{50}, rat (g/kg)	Dermal LD_{50}, rabbit (g/kg)	Reference
No. 6 Heavy fuel oil, API 78-6	> 25.0	> 4.94	API, 1980c
No. 6 Heavy fuel oil, API 78-7	> 25.0	> 5.0	API, 1980a
No. 6 Heavy fuel oil, API 78-8	> 24.7	> 5.0	API, 1980d
No. 6 Heavy fuel oil, API 79-2	5.13	> 5.35	API, 1980b
Catalytically cracked clarified oil (CCCO), API 81-15	4.32	> 2.0	API, 1982
Steam-cracked residue, carbon black	> 2.0	> 2.0	DSM Kunststoffen, 1989a DSM Kunststoffen, 1989b

The data show that heavy fuel oils are of a low order of toxicity following acute oral, or dermal exposure.

Acute dermal LD_{50} values in rabbits were above 2 g/kg for all samples following a single application of test sample to the clipped skin for 24 hours. The animals were observed for 14 days. In this period, 3 of 8 animals died when treated at a dose of 5.35 g/kg with No. 6 Heavy fuel oil (API, 1980b). No deaths occurred in the other studies (API, 1980a; API, 1980c; API, 1980d; API, 1982; DSM Kunststoffen, 1989b). Slight erythema was noted in the test area for a few animals (API, 1980c).

There are no data available for inhalation studies on heavy fuel oils. Inhalation of heavy fuel oil (vapour or aerosol) by humans has not been reported and is unlikely due to the very low vapour pressures of the materials.

4.2.2. Irritancy and sensitization

Skin and eye irritancy and skin sensitization data are summarized in **Table 4**.

Table 4: Summary of skin irritation, eye irritation, and skin sensitization data for heavy fuel oils

Material	Skin Irritation	Eye Irritation	Skin Sensitization	Reference
No. 6 Heavy fuel oil, API 78-6	minimal	minimal	negative	API, 1980c
No. 6 Heavy fuel oil, API 78-7	slight	minimal	negative	API, 1980a
No. 6 Heavy fuel oil, API 78-8	minimal	mild	negative	API, 1980d
No. 6 Heavy fuel oil, API 79-2	slight	mild	negative	API, 1980b
Catalytically cracked clarified oil (CCCO), API 81-15	slight	slight	negative	API, 1982 API, 1984
Steam-cracked residue, carbon black oil (DSM Roetolie)	moderate	slight	ND	DSM Limburg, 1989a DSM Limburg, 1989b

ND = Not Determined

All of the skin irritation studies have been performed using 24-hour Draize tests using occluded patches, and in all cases, minimal to moderate skin irritation resulted.

None of the heavy fuel oils or components was an eye irritant. Furthermore, API No. 6 heavy fuel oils and CCCO were not skin sensitizers in tests using a Buehler technique.

4.3. SUBACUTE/SUBCHRONIC STUDIES

No subacute/subchronic oral studies have been reported but a number of studies have investigated the effects of heavy fuel oils following repeated application to the skin for periods from 12 days to 13 weeks.

4.3.1. Dermal studies

In a series of studies with No. 6 heavy fuel oils, the following results were obtained following repeated dermal application to rabbits (5 days of treatment, 2-day rest period, and 5 additional days of treatment):

a) API 78-6, API 78-7, and API 78-8, at doses of 8.0 ml/kg/day, resulted in severe dermal irritation and injury at the treatment sites and there was 25% mortality. Histopathological examination of the tissues from the treated rabbits revealed evidence of dermal and hepatic toxicity and proliferative changes in the transitional epithelium of the urinary bladder. These changes were attributed to exposure to the test substance (API, 1980a; API, 1980c; API, 1980d).

b) API 79-2, at doses of 1.0, 2.0, and 2.5 ml/kg/day, resulted in significant skin irritation at the treatment sites. The major systemic effect was multifocal necrosis of the liver, which occurred at all doses. Centrilobular vacuolar degeneration was also found (API, 1980b).

In a series of repeat dermal application studies conducted on CCCO, the following results were obtained:

a) Doses of 8, 30, 125, and 500 mg/kg/day were applied five times per week for 13 weeks to the shorn backs of Sprague-Dawley rats. A 2000 mg/kg/day dose was applied to one test group for a 2-week exposure. Dose-related mortality and depression of body weight gain occurred in animals treated at doses of 30 mg/kg/day or greater. The prime target organs for toxicity were the liver, thymus, and bone marrow. Serum chemistry and enzymological changes were also observed following exposure. These effects appear to be due to absorption of carbazoles, which are readily bioavailable in animals by the dermal route (McCullough, 1985; Cruzan et al; 1986).

b) Doses of 200, 1000, and 2000 mg/kg/day (API 81-15) were applied 3 times per week to the backs of rabbits for 28 days. Three treatment-related deaths occurred, two in the high-dose group and one in the middle-dose group. Liver enlargement was found. Significantly reduced body weight gains were seen at high and middle doses. Skin irritation ranged from moderate (low dose) to severe (middle and high doses) with skin ulceration (API, 1983).

c) Doses of 400, 1000, and 4000 mg/kg/day (API 81-15) were applied 5 times per week to the backs of Fischer 344 rats for 28 days. Twelve treatment-related deaths occurred; 5/10 at 4000 mg/kg/day, 2/10 at 2000 mg/kg/day, 4/10 at 1000 mg/kg/day, and 1/10 at 400 mg/kg/day. Significantly increased liver weights were found at 400 and 1000 mg/kg/day. Histopathology was performed on the control group and 400 mg/kg/day group. Slight to moderate diffuse hepatomegaly and minimal to slight skin irritation was found at 400 mg/kg/day (API, 1986a).

d) Doses of 40, 200 and 400 mg/kg/day (API 81-15) were applied 5 times per week to the shorn backs of Fisher 344 rats for 12 weeks. The study was planned for 90 days, but was terminated at 28 days for the highest dose group and at 84 days for the other two test groups due to excessive mortality. General systemic toxicity was found, as evidenced by reduced body weight gains, reduced haematology indices, elevated enzyme levels, and significantly increased liver weights (API, 1985e).

4.4.   CARCINOGENICITY

The carcinogenicity of heavy fuel oils has been evaluated in a series of mouse skin painting studies. These studies are summarized in **Table 5**.

Table 5:   Summary of mouse skin carcinogenicity studies with heavy fuel oil components

Material Tested	Dosing Regime (No. of animals)	Duration	Result	Mean latency (weeks)	Ref.
Steam-cracked tar	15 mg 3 X week (100)	> 2 years	38/62 tumours	43	Smith et al, 1951
Catalytically-cracked clarified oil (CCCO)	25 µl 3 X week (40)	> 2 years	36/40 tumours	17	McKee et al, 1990
Catalytically-cracked clarified oil (CCCO) API 81-15, 10% in toluene	50 µl 2 X day (100)	> 2 years	49/50 tumours (48 malignant; 1 benign)	22	API, 1989a
Catalytically-cracked clarified oil (CCCO) API 81-15, 1% in toluene	50 µl 2 X day (100)	> 2 years	45/50 tumours (44 malignant; 1 benign)	72	API, 1989a
Catalytically-cracked clarified oil (CCCO) API 81-15, 0.1% in toluene	50 µl 2 X day (100)	> 2 years	2/50 tumours (2 benign)	113	API, 1989a

Six fractions, derived by distilling steam-cracked tar were evaluated in lifetime dermal carcinogenicity studies. In these studies steam-cracked tar was a dermal carcinogen with those fractions distilling above 370 °C being the most carcinogenic (Smith et al, 1951).

CCCO has long been recognized by the petroleum industry as a potent dermal carcinogen. It is commonly used as a positive (tumour-producing) control material in dermal carcinogen studies. All lifetime skin painting studies carried out with >1% CCCO have resulted in skin cancers in the majority of animals.

4.5.   TUMOUR INITIATING/PROMOTING ACTIVITY

Dermal bioassays were conducted to assess the tumour initiation and promotion potential of CCCO (API 81-15). The CCCO was applied at a concentration of 1.0% in toluene. In the initiation phase, 30 mice were dosed dermally once a day for 5 consecutive days with 50 µl of 1.0% CCCO in toluene. After a 2-week rest period, all mice were then dosed twice weekly for 25 weeks with PMA (phorbol-12-myristate-13-acetate), a known tumour promotor (API, 1989b). Under the conditions of this study, significant initiation activity was detected (26/30 tumors, mean latency of 16 days).

In the promotion phase, CCCO failed to increase the incidence of animals with histologically confirmed tumours. However, a statistically significant increase in the

number of animals with grossly observed masses and shortened latency time was observed, suggesting possible weak promoting activity (API, 1989b).

4.6. GENOTOXICITY

A number of heavy fuel oil components have been assessed for genotoxic activity in *in vitro* microbial mutation assays, microbial cytogenetics assays, mouse lymphoma assays, *in vitro* and *in vivo* sister chromatid exchange assays, and *in vitro* and *in vivo* unscheduled DNA synthesis assays. The results of the studies are summarized in **Table 6**.

4.6.1. *In vitro* assays

In vitro bacterial mutagenicity assays (BMA) have been carried out on heavy fuel oil components with S9 metabolic activation, and in all cases, the materials have been shown to be mutagenic (API, 1986b; Feuston et al, 1994).

In addition to BMA, other *in vitro* mutagenicity assays have been conducted on catalytic cracked clarified oil (API 81-15). The results were as follows:

a) In the mouse lymphoma assay (MLA), dose-dependent increases in mutant frequency were found in the presence of S9 metabolic activation over the concentration range 1.95 to 31.3 nl/ml. Toxicity was noted at all levels, and survival was less than 10% at concentrations exceeding 3.9 nl/ml. In the absence of S9, evidence of weak mutagenicity was found at 125 nl/ml (API, 1985a).

b) In the sister chromatid exchange assay (SCE) significant increases in SCEs were found in the presence of S9 over the concentration range tested. In the absence of S9, SCE levels were not significantly elevated (API, 1985b).

c) The Chinese hamster ovary (CHO)/Hypoxyanthine-Guanine Phosphoribosyl transferase (HGPRT) mammalian cell forward gene mutation assay was conducted at 5 concentrations. No dose-dependent increases in mutant frequencies were observed, either in the presence or absence of S9 (API, 1985b).

d) Rat liver cells were exposed to 6 noncytotoxic concentrations of the test substance in an unscheduled DNA synthesis (UDS) study. Significant increases above the solvent control values were observed, both for unscheduled DNA synthesis and in the percentage of cells in repair (API, 1985d).

e) In the cell transformation assay (CTA), there were no significant increases in morphological transformation frequency when mouse embryo cells were exposed to CCCO at four concentrations for 3 days without activation. In the presence of S9, there was a significant increase in transformation frequency at 100 μg/ml test substance following exposure for four hours. However, low survival rates were found at treatment levels above 100 μg/ml in the presence of S9 (API, 1986c).

4.6.2. *In vivo* assays

Four *in vivo* mutagenicity assays have been reported for CCCO (API 81-15). The results were as follows:

a) In the SCE assay, the test substance produced a small but significant dose-dependent increase in mouse bone marrow SCEs compared to the control (API, 1985f).

b) In the UDS assay on primary rat liver cultures, the results were positive at 200 mg/kg (after 12 hours but not after 2 hours) and at 1000 mg/kg (after both 2 and 12 hours). Unscheduled DNA synthesis, as measured by the amount of incorporated tritiated thymidine, was significantly elevated in a dose-dependent manner (API, 1985c).

c) In the mouse embryo limb bud culture (MELB), 3 groups of rats were fed 0.1, 0.3, and 1.0 g/kg daily for 5 days. The test substance did not significantly increase the frequency of chromosomal aberrations, nor did it increase the mitotic index in male and female bone marrow cells at any dose (API, 1995).

d) In the bone marrow cytogenetics assay the results were negative after the daily intraperitoneal administration of CCCO to male and female rats at doses of 0.1, 0.3 & 1.0 g/kg/day.

Table 6:   Genotoxicity studies with heavy fuel oil components

Material	Test System	Results With Activation (S9)	Without Activation (S9)	Reference
In-vitro studies				
API 81-15	Bacterial mutagenicity	Positive	ND	API, 1986b
API 81-15	Mouse lymphoma	Positive	Weak positive	API, 1985a
API 81-15	Chinese hamster ovary	Negative	Negative	API, 1985b
API 81-15	Cell transformation	Ambiguous	Ambiguous	API, 1986c
API 81-15	Sister chromatid exchange	Positive	Positive	API, 1985f
API 81-15	Unscheduled DNA synthesis	ND	Positive	API, 1985d
Clarified slurry oil	Bacterial mutagenicity	Positive	ND	Feuston et al, 1994
Heavy coker gas oil	Bacterial mutagenicity	Positive	ND	Feuston et al, 1994
Heavy vacuum oil	Bacterial mutagenicity	Positive	ND	Feuston et al, 1994
Syntower bottoms	Bacterial mutagenicity	Positive	ND	Feuston et al, 1994
Visbreaker gas oil	Bacterial mutagenicity	Positive	ND	Feuston et al, 1994
in vivo studies				
API 81-15	Bone marrow cytogenetics	Negative	ND	API, 1985a
API 81-15	Mouse embryo limb bud	Negative		API, 1995
API 81-15	Sister chromatid exchange	Positive		API, 1985g
API 81-15	Unscheduled DNA synthesis	Positive		API, 1985c

4.7. DEVELOPMENTAL AND REPRODUCTIVE TOXICITY

The developmental and reproductive toxicities of heavy fuel oil components have been investigated in several studies.

Sprague-Dawley rats were dermally exposed for 19 days (from day 0 of gestation) to 4, 8, 30, 125, and 250 mg/kg/day of CCCO. Each group contained 10 pregnant females. Signs of maternal toxicity, seen at doses as low as 8 mg/kg/day, included vaginal bleeding, decreased body weight gain, reduced food consumption, increased relative liver weights, thymic atrophy, aberrant serum chemistry, and death. The number of fetal resorptions was markedly increased, and the number of viable offspring decreased, by CCCO exposure at doses of 30 mg/kg/day and greater. The group receiving 250 mg/kg/day carried no viable offspring. Abnormal external development was observed in living and dead fetuses exposed *in utero* to CCCO at dose levels of 8 mg/kg/day and greater (Feuston et al, 1989).

Four other heavy fuel oil components have been assessed for developmental and reproductive toxicity. In these studies, the materials were applied dermally to the pregnant Sprague-Dawley rats from day 0 to 19 of gestation:

a. Clarified slurry oil was applied at doses of 0, 4, 8, 30, 125, and 250 mg/kg/day. The lowest observed adverse effect (LOAEL) was 30 mg/kg/day. The foetal resorption was 69.9% at this dose (Feuston et al, 1994).

b. Heavy coker oil was applied at doses of 0, 8, 125, 250 mg/kg/day with a LOAEL of 125 mg/kg/day. The foetal resorption was 78.0% (Feuston et al, 1994).

c. Heavy vacuum gas oil was applied at doses of 0, 30, 125, 500, 1000 mg/kg/day with a LOAEL of 500 mg/kg/day. The foetal resorption was 35.1% at this dose (Feuston et al, 1994).

d. Syntower bottoms was applied at doses of 0, 4, 8, 30, 125 mg/kg/day with a maternal LOAEL of 8 to 30 mg/kg/day. The foetal resorption rate is not indicated, but the authors suggested that although the resorption rate was not statistically significant at 8 mg/kg/day, they considered it to be biologically significant (Feuston et al, 1994).

In the studies profiled above, observed signs of toxicity included increased mortality, decreased body weights, decreased thymus weight, increased liver weight, aberrant serum chemistry and haematology, increased incidence of resorption, and decreased foetal body weight (Feuston et al, 1994).

To evaluate teratogenic effects as a function of gestation day, groups of Sprague-Dawley rats received either a single oral dose (2000 mg/kg) of clarified slurry oil or syntower bottoms on one of gestation days 11 - 14. Additionally, to evaluate effects as a dose response function, rats received a single oral dose of clarified slurry oil or syntower bottoms on gestation day 12 at 125, 500, and 2000 mg/kg. On gestation day 20, dams were sacrificed and foetuses evaluated for normal development. Maternal toxicity was observed for both clarified slurry oil and syntower bottoms at 500 mg/kg and higher. The incidence of resorption was greatest on gestation day 11. A common pattern of malformation was observed which included cleft palate, diaphragmatic hernia, and paw and tail defects. The percentage and type of malformation observed was influenced by the day of exposure during gestation (Feuston et al, 1991).

A study was conducted to evaluate potential adverse reproductive effects in male and female rats when clarified slurry oil was administered by the dermal route of exposure. Clarified slurry oil was administered to male rats at doses of 0, 0.1, 1, 10, 50, and 250 mg/kg/day, and to female rats at the same dosages for 14 days prior to a 7-day cohabitation period and continuing to day 0 of gestation. Under the conditions of this experiment, the no-observable-adverse-effect-level (NOAEL) for clarified slurry oil in male rats was 1 mg/kg/day. The reproductive NOAEL for male rats was >250 mg/kg/day. The NOAEL for female rats was 10 mg/kg/day and the reproductive NOAEL was > 250 mg/kg/day. Clarified slurry oil did not produce any adverse effects on the male or female fertility parameters (Hoberman et al, 1995).

5. HEALTH ASPECTS

5.1. EFFECTS IN MAN

Where proper precautions are taken, health risks for individuals are minimal, particularly bearing in mind the closed systems in which fuel oils are normally handled and used.

5.2. INHALATION

Mist and vapours will be evolved from heavy fuel oils at the elevated temperatures encountered in storage and use and these are likely to cause eye and respiratory irritation. However, such exposure is minimal under normal use conditions and significant exposure is most likely during maintenance operations; in undertaking the latter, adequate personal protective equipment must be worn.

Hydrogen sulphide may be evolved from fuel oils under certain conditions such as elevated temperatures. It is highly toxic, causing effects which include eye irritation, nervousness, nausea, headache, insomnia and, in severe cases, unconsciousness and death. Hydrogen sulphide can also paralyse the olfactory system, making it inadvisable to rely on detecting its odour as a warning of its presence.

5.3. INGESTION

Given the nature of residual fuel oil and the fact that it is normally handled hot, its ingestion must be regarded as highly improbable. However, in the unlikely event of it happening, spontaneous vomiting would be expected to occur. There could also be irritation of the gastro-intestinal tract.

5.4. ASPIRATION

Because of the high viscosity of fuel oil, direct aspiration into the lungs is only a remote possibility (Gerarde, 1963).

5.5. SKIN CONTACT

Because of the high handling temperatures, particularly with the heavy grades, a major hazard is the possibility of skin burns. However, this possibility, together with the unpleasant smell and colour of the fuel, provides a deterrent against direct skin contact.

Nevertheless, where exposure arises and precautions and personal hygiene are poor, there is the possibility firstly of skin and eye irritation of a relatively mild nature, and secondly of dermatitis on more prolonged contact either directly on the skin or via fuel-soaked clothing.

Prolonged or repeated skin contact, particularly under conditions of poor personal hygiene, may lead to effects ranging from dry skin with irritation to oil acne and oil

folliculitis. Some individuals may be particularly susceptible to skin cracking and dermatitis.

With exposure under such conditions, in rare cases serious disorders such as skin cancer could eventually occur. This is because blended materials may contain carcinogenic components. Since the person concerned is very unlikely to know the composition of the fuel oil to which he may be exposed, the handling procedures for any fuel oil should be adequate to protect against their potentially carcinogenic effect.

5.6.   EYE CONTACT

Eye contact from splashes or high mist levels is likely to cause irritation.

6. EXPOSURE LIMITS

No occupational exposure limits have been established for heavy fuel oil. Nevertheless, it is advisable to reduce exposure to heavy fuel oil mist or vapour to a minimum.

However, one of the constituents of heavy fuel oil vapours can be hydrogen sulphide which can accumulate in storage tank head spaces. Exposure limits set for hydrogen sulphide by various agencies are listed in **Table 7.**

Table 7: Occupational exposure limits for hydrogen sulphide.

Agency/Country	8-hour TWA	15 min STEL	Reference
ACGIH	14 mg/m^3	21 mg/m^3	ACGIH , 1996
France	7 mg/m^3	14 mg/m^3	INRS, 1993 INRS, 1995
Germany	15 mg/m^3	15 mg/m^3 (Ceiling)	DF, 1996
Netherlands	15 mg/m^3	None established	MAC, 1996
Sweden	14 mg/m^3	20 mg/m^3 (Ceiling)	AFS, 1996
UK	14 mg/m^3	21 mg/m^3	UK HSE, 1997

Notes:

ACGIH   American Conference of Governmental Industrial Hygienists.

TWA   Time weighted average for an 8-hour day and 40 hour week.

STEL   Short - term exposure limit over a 15 min period.

7.   HANDLING ADVICE

Heavy fuel oils are stored and handled in closed systems and involve the use of insulated storage tanks and lagged and trace-heated transfer lines. Exposure to fuel oil is therefore limited, except on tank filling and during maintenance operations. It is recommended that the following advice be observed:

- Individuals handling or using heavy fuel oils should be advised of the hazards, proper procedures and precautions, including health effects and recommendations for emergency treatment. Safety data sheets should be obtained from the suppliers.

- Storage tanks in land based applications should be surrounded by oil tight bund walls to prevent escape of heavy fuel oil into the environment in the event of a major spillage or tank failure.

- In the event of a spillage, absorb or contain liquid with sand, earth or other spill control material. Prevent from entering drains, ditches or waterways. If this cannot be done, inform local authorities.

- A marine spillage should be reported to the nearest coastal state and additional guidance sought from the owner of the vessel, or the charterer.

- The cleaning, inspection and maintenance of storage tanks is a specialist operation which requires the implementation of strict confined-space entry procedures. These include the issuing of permits, gas-freeing of tanks, use of manned harness and lifeline, and wearing air-supplied breathing apparatus.

- The headspaces of fuel oil storage tanks should be considered as hazardous and potentially flammable (see Section 10). Electrical equipment within the space must meet the appropriate safety standards.

- Prior to entry into a tank, the atmosphere in the tank should be monitored using an oxygen meter and/or an explosimeter. In addition, appropriate electrochemical sensors or indicator tubes must be used to check for the presence of hydrogen sulphide.

- Fuel storage temperatures may be up to 50°C, line transfer temperatures up to 55°C and fuel atomisation temperatures up to 130°C depending on the grade of fuel being used. Precautions should be taken to avoid skin burns from unprotected pipelines and equipment components.

- Skin contact with heavy fuel oil should be avoided during transfer operations and maintenance work by wearing impervious gloves e.g. of nitrile rubber or PVC.

- A full-face shield should be worn if splashes are likely to occur.

- Overalls should be used to minimise contamination of personal clothing. Chemical resistant safety shoes or boots should be worn.

- The cleaning of combustion deposits from boilers and furnaces is a specialist operation; suitable breathing apparatus must be used to prevent the inhalation of dust and ash.

8. EMERGENCY TREATMENT

Symptoms and effects:

Exposure to hydrogen sulphide at concentrations above the recommended occupational exposure standard may cause headache, dizziness, irritation of the eyes, upper respiratory tract, mouth and digestive tract, convulsions, respiratory paralysis, unconsciousness and even death. Unconsciousness as a result of exposure to hydrogen sulphide may occur extremely rapidly and without other symptoms.

Contact with hot product may cause skin burns, including tissues underlying the skin. Owing to its high viscosity, this product does not normally constitute an ingestion hazard. Ingestion will only occur in grossly abnormal circumstances. If ingested, it can lead to irritation of the mouth, throat and digestive tract; vomiting may also occur. Aspiration into the lungs may occur directly or following ingestion. This can cause chemical pneumonitis which may be fatal. Prolonged exposure to vapour/mist concentrations may cause headache, dizziness, nausea, asphyxiation, unconsciousness and even death.

Protection of first aiders:

Wear self-contained breathing apparatus if presence of hydrogen sulphide is suspected.

First Aid – Inhalation:

Remove to fresh air. If breathing but unconscious, place in the recovery position. If breathing has stopped, apply artificial respiration. If heartbeat absent give external cardiac compression. Monitor breathing and pulse. OBTAIN MEDICAL ATTENTION IMMEDIATELY.

First Aid – Skin:

If high pressure injection injuries occur, obtain medical attention immediately. In the case of burns, wash skin thoroughly with water using soap if available. Do not use kerosine, gasoline or solvents. Contaminated clothing must be removed as soon as possible. It must be laundered before reuse. If persistent irritation occurs, obtain medical attention.

First Aid – Eye:

Flush eye with water. If persistent irritation occurs or if there is any suspicion of damage from hot product, obtain medical attention immediately.

First Aid – Ingestion:

Do not induce vomiting. Protect the airway if vomiting begins. Give nothing by mouth. If breathing but unconscious, place in the recovery position. If breathing has stopped, apply artificial respiration. DO NOT DELAY, OBTAIN MEDICAL ATTENTION IMMEDIATELY.

Advice to physicians:

Treat symptomatically.

- High-pressure injection injuries require early surgical intervention and possible steroid therapy to minimise tissue damage and loss of nerve function. X-ray examination is required to assess the extent of the injury. Local anaesthetics or hot soaks should not be used with such injuries since they can contribute to local swelling, vasospasm and ischaemia. Prompt surgical decompression, debridement and evacuation of foreign bodies should be carried out under general anaesthetic. Because injected material may be deposited at some distance from the point of injection, wide exploration is essential.

- Prolonged exposure to high concentrations of hydrogen sulphide may lead to a delayed chemical pneumonitis and/or pulmonary oedema. In cases of excessive inhalation, observe in hospital for 48 hours for signs of pulmonary oedema.

- Diagnosis of ingestion of this product is by the characteristic odour on the victim's breath and from the history of events. In cases of ingestion, consider gastric lavage. Gastric lavage must only be undertaken after cuffed endotracheal intubation in view of the risk of aspiration.

- In cases of chemical pneumonitis, antibiotic and corticosteroid therapy should be considered.

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9.　DISPOSAL

Heavy fuel oils are primarily used as fuels for combustion and disposal as waste is seldom necessary. When it is required to dispose of fuel oil, for example, following a spillage or tank cleaning operations, this should be done through a recognised waste contractor. In marine applications, all waste fuel oil should be collected and disposed of on land in accordance with local regulations.

Advice on the handling of waste or spilled material can be obtained from previously published CONCAWE reports (CONCAWE 1980; 1981; 1983, 1988).

10.   FIRE AND EXPLOSION HAZARDS

Heavy fuel oils have flash points above 55°C (Pensky Marten Closed Cup method) and are not therefore classified as flammable. Flammability limits for fuel vapour/air mixtures lie between approximately 1.0 to 6.0 % (V/V); autoignition temperatures are in the range of approximately 220 to 300°C. Ignition of heavy fuel oils at ambient temperature may be difficult, but if ignited at elevated temperatures, the product will burn.

However, despite not being classified as flammable, heavy fuel oils are capable of producing light hydrocarbon vapours in a tank head space at concentrations in the flammable range (OCIMF 1989). This can occur even when the temperature of the liquid is below the flash point. In consequence, it is recommended that the head space of all heavy fuel oil tanks should be considered potentially flammable and appropriate precautions taken.

In designing heavy fuel oil installations, it is also important to ensure that heating elements and their corresponding thermostats are always placed below the level of the tank draw-off line so that they never become uncovered by fuel oil during normal operations. If they do become uncovered, there could be a danger of an explosion and subsequent fire from fuel oil contacting over-heated elements or heating coils.

11.   ENVIRONMENTAL HAZARDS

Heavy fuel oils are composed of residual materials blended with middle distillates, or cutter stocks of lower molecular weight, and their composition is highly variable. As a result, the ecotoxicity associated with these oils varies depending on the nature and proportion of the added middle distillates. The following review collects together the available data on the environmental effects of heavy fuel oils based both on laboratory studies and observations following accidental spillages.

11.1.   PHYSICAL/CHEMICAL CHARACTERISTICS

The aqueous solubilities of all the components of heavy fuels are very low with the lower molecular weight components of the middle distillate cutter stocks showing the greatest solubilities, particularly the aromatic hydrocarbons. However, on release to the environment, these same constituents will show the greatest tendency to be lost by volatilisation, since they have the highest vapour pressures at ambient temperatures. Log K_{ow} (octanol/water partition coefficient) values of heavy fuel oil components range from 2.7 to over 6 suggesting that they may have a tendency to bioaccumulate.

11.2.   PERSISTENCE AND BIODEGRADATION

Upon release into the environment, heavy fuel oil will break into small masses and will not spread as rapidly as less viscous oil (Petersen, H.C., 1978; Fremling, C.R., 1981; Wolfe, D.A., 1977; Grose, P.L. et al, 1979). The density of some heavy fuel oils means that they may sink on release to water, rather than float on the surface like other petroleum fuels. Loss of the lower molecular weight components due to volatility and dissolution will increase the density of the floating oil, causing it to sink. This heavy fraction will assume a tar-like consistency and stick to exposed substrates or become adsorbed to particulates. Weather conditions and temperature during the period after the spill will significantly influence the rate of dispersion; wind and wave action will tend to disperse oil into the water column, whilst higher temperatures will increase the rate of evaporation of lighter hydrocarbons. Water temperature is a major factor in determining the extent of the environmental impact following a heavy fuel oil spill since higher temperatures will enhance loss of lighter constituents by evaporation as well as degradation processes.

Sedimentation has been shown to be an important mechanism for removal of heavy fuel oil from the water column following some spills. During the second week following a spill of No. 5 fuel oil from the Soviet tanker Tsesis in 1977, 0.7% of sediment collected at the site was fuel oil adsorbed to detritus or clay particles (Johansson, S. et al, 1980; Linden, O. et al, 1979). In all, 30-60 tons of the oil remaining after cleanup at this site was transported to the bottom by sedimentation.

The composition of heavy fuel oil will change drastically during weathering. Initially, a rapid loss of the low molecular weight components by evaporation, dissolution and biodegradation will occur, resulting in almost complete removal of n-alkanes up to C_{17} in the first year following a spill (Kolpack, R.L. et al, 1978; Guard, H.E. and Cobet, A., 1972; Petersen, H.C., 1978; Vandermeulen, J.H. et al, 1977; Rashid, M.A., 1974; Cretney, W.J. et al, 1978). The more recalcitrant pristane and phytane will be biodegraded slower, but should be degraded in a few years. The branched chain alkane components will be the most resistant to degradation and will persist for many years (Song, H. et al, 1990). In 28 day laboratory studies with crude and

refined oils, Bunker C was the least degraded (11% compared to 51-82% for crudes) due to its higher proportion of high molecular weight aromatics (Walker, J.D. et al, 1976; Geyer, R.A., 1980; Mulkins-Phillips, G.J. and Stewart, J.E., 1974). This slow rate of degradation has also been observed in the field (Kolpack, R.L. et al, 1978; Petersen, H.C., 1978; Wolfe, D.A., 1977; Rashid, M.A., 1974; Geyer, R.A., 1980).

Bunker C from the Arrow spill could still be found in the subsurface sediments and on some shorelines up to 7 years after the spill (Rashid, M.A., 1974; Vandermeulen, J.H. and Gordon Jr., D.C., 1976; Keizer, P.D. et al, 1978). Oil removal was occurring fastest in areas with heavy wave action and slowest at high tidal areas in sheltered locations (Wolfe, D.A., 1977; Rashid, M.A., 1974; Strand, J.A. et al, 1992). Covering of oil through bioturbation and sediment accumulation were more effective removal mechanisms for this tar-like residue than biodegradation (Kolpack, R.L. et al, 1978; Baker, J.M. et al, 1993). Resuspension of these residues could lead to contaminant spread and continued impact on benthic and interstitial organisms.

11.3.   TOXICITY - AQUATIC AND TERRESTRIAL

Acute toxicity data for heavy fuel oils to a variety of aquatic species are summarized in **Table 8**. The relative sensitivities of these species are difficult to compare, since a variety of fuel oils (with different types and quantities of cutter stock) and test procedures were used. For assessment of the ecotoxicity of poorly water soluble mixtures of hydrocarbons like petroleum fuels, it is now generally accepted that studies should be carried out using water accommodated fractions (WAF), and the results expressed in terms of loading rate (Girling, A. et al, 1992). The loading rate is defined as the ratio of test material to water used in the preparation of the aqueous test medium. Most data in the literature, however, come from experiments in which water-soluble fractions (WSF), prepared by mixing a large volume of fuel oil with water, are diluted with further water to produce the test media. Results from these studies are then expressed in terms of dilution (as % dilution of the WSF) and/or as the measured hydrocarbon concentration that causes the specified level of effect. In neither case is it possible to convert the reported result to the amount of product that must be added to the culture medium to produce the effect. These issues are discussed in more detail elsewhere (CONCAWE, 1992).

Few studies have been reported in which toxicity has been assessed using water accommodated fractions (WAF). However, a series of studies on the acute (short-term) toxicity of WAF of two heavy fuel oil samples to fish, daphnia and algae were recently carried out by a single laboratory (Eadsforth, 1997a; 1997b). The loading rate results indicate that the acute aquatic toxicities to fish (96 hour toxicity to Rainbow trout) and daphnia (48 hour immobilisation of *Daphnia magna*) were all greater than 100 mg/l, and often significantly greater. Algae (*Raphidocelis subspicata*) were somewhat more susceptible to the effects of heavy fuel oils, with 72-hour inhibitory effect EL_{50} levels (expressed as either specific growth rate - SGR, or biomass assessed as area under growth curve - AUC) generally in the range 30-100 mg/l.

Literature data on aquatic toxicity, usually expressed in terms of dissolved hydrocarbons or % WSF, can provide a useful indication of the level of toxicity expected following release of heavy fuel oil to the aqueous environment. In general, data for No. 6 fuel oil without cutter stock indicate that this fuel is essentially non-toxic to a variety of organisms (Giddings, JM et al, 1980; Mobil Oil Corporation, 1987). However, a wide range of LC_{50} values are seen for blended fuels (LC_{50} values, expressed in terms of dissolved hydrocarbons, in the range 0.9 to 2417

ppm); these products may contain a higher proportion of lower molecular weight hydrocarbons.

Additional laboratory studies have been run to evaluate the sublethal effects of heavy fuel oil on aquatic organisms. Serum glucose level reduction and slight damage to gill morphology were observed following exposure of rainbow trout (*Salmo gairdneri*) with up to 200 mg/l of Bunker C for 96 hours (McKeown, B.A. and March, G.L., 1978a). The effect of this oil greatly increased when mixed with a dispersant. Sheepshead minnow (*Cyprinodon variegatus*) exposed to Bunker C showed a difference in respiratory rate and a depression of oxygen consumption (Anderson, J.W. et al, 1974b). The intermolt period for juvenile horseshoe crabs (*Limulus polyphemus*) showed a linear increase with increasing exposure concentration to Bunker C (Strobel, C.J. and Brenowitz, A.H., 1981). American oysters (*Crassostrea virginica*) showed an ability to close their shell to minimize Bunker C exposure (Anderson, R.D. and Anderson, J.W., 1976).

Studies with coral, sea anemone and a zoanthid were performed by immersing the animals in straight oil for a period of time with subsequent return to clean water (Wicksten, M.K., 1984; Reimer, A.A., 1975b; Reimer, A.A., 1975a; Birkeland, C. et al, 1976). Certain species of coral can survive short exposures (5 to 30 minutes) to straight Bunker C (**Table 9**) (Reimer, A.A., 1975b). Bunker C appears to affect the feeding behaviour of the zoanthid *Palythoa variabilis*, since animals could not discriminate between inert and chemically active particles for some time after being exposed (Reimer, A.A., 1975a). Mucus secretions by these marine species may be reducing the impact of the oil.

High levels of petroleum hydrocarbons were found in the gills, liver and kidney of rainbow trout (*Salmo gairdneri*) exposed to chlorine-labelled Bunker C (McKeown, B.A. and March, G.L., 1978b). A 20-fold increase in the levels was noted when a dispersant was used in combination with the Bunker C. Metabolism within the fish may be accounting for the elevated levels in the kidney and liver, since a linear increase with increasing exposure concentration was only observed in the muscle. A similar effect was noted in the field following accidental spills. Hydrocarbon levels in mussels (*Mytilus edulis*) rapidly increased for 60 days after the spill and then rapidly decreased (Lee, R.F. et al, 1981; Boehm, P.D. et al, 1982). One year after the spill, tissue concentrations remained elevated relative to background levels; preferential n-alkane degradation appears to be occurring in the tissues. The deposit-feeding clam (*Macoma balthica*) showed a rapid but modest increase in hydrocarbon levels after the Tsesis spill. Unlike the mussel, however, little depuration was observed, possibly due to reintroduction of petroleum-bearing particulates from the benthic sediments (Boehm, P.D. et al, 1982). A similar effect was observed with the clam (*Mya arenaria*) following the Arrow spill in Chedabucto Bay (Vandermeulen, J.H. et al, 1977).

A variety of effects have been observed in the field following spills of heavy fuel oils. In general, littoral and supralittoral species are the most likely to be initially impacted by the oil, but the fastest recovery is seen in these organisms (Linden, O. et al, 1979; Geyer, R.A., 1980; Thomas, M.L.H., 1978; Thomas, M.L.H., 1973; Chan, G.L., 1974; Chan, G.L., 1972). After a tanker collision and spill in San Francisco Bay, 4.2-7.5 million intertidal invertebrates were estimated to have been smothered by oil (Chan, G.L., 1977). Three years after the spill, recruitment for many species had returned to normal, although species diversity has been impacted. Highly mobile organisms are able to recolonize the area faster than animals with lower mobility (Geyer, R.A., 1980; Notini, M., 1978). A similar effect was noted in the littoral habitat following the

Arrow spill in Chedabucto Bay, Nova Scotia (Thomas, M.L.H., 1978; Thomas, M.L.H., 1973).

Water column phytoplankton biomass and primary production may be stimulated after a spill of heavy fuel oil. (Linden, O. et al, 1979; Kineman, J.J. et al, 1980); this may be caused by a decrease in zooplankton grazing. Ingestion of oil droplets by zooplankton and incorporation of the oil in faecal pellets has been shown (Johansson, S. et al, 1980; National Research Council, 1985; Soule, D.F. et al, 1978). Following the spill from the Liberian tanker, Arrow in Chedabucto Bay, Nova Scotia in 1970, 10% of the oil was associated with zooplankton and 20% of the remaining oil was delivered to the bottom sediments as faecal pellets. No impact on fish was observed following spills, possibly due to avoidance of the impacted area. Benthic organisms are the most susceptible to long-term effects following a spill. Ten months after the Tsesis spill, no sign of recovery of benthic organisms was observed (Linden, O. et al, 1979). Results from this study indicate that deeper soft bottom sediments and their resident aquatic life are more vulnerable to this oil than other systems.

The only terrestrial studies of heavy fuel oil which could be located dealt with the impact on representative marsh grasses. The season of the year strongly influenced the degree of damage observed. Marsh cordgrass (*Spartina alterniflora*) oiled over the winter months following the Arrow spill showed no effect in the spring when the plant shoots penetrated the oil (Wolfe, D.A., 1977). During the summer, warming and subsequent remobilization of the oil led to increased exposure. The following year, reduced numbers of plants were observed with total recovery in subsequent years. This has been observed in other locations, where heavy mortalities have been observed during the first year after a spill, with recovery evident in 2 years and normal population growth after 5 years (Baker, J.M. et al, 1993; Thomas, M.L.H., 1978; Roland, J.V. et al, 1977; Webb, J.W. et al, 1981) Cattails (*Typha* sp.), showed a similar resistance to oil penetration and toxicity (Alexander, M.M. et al, 1978).

Physical entrapment of birds and coating of feathers with tarry residue following spills has been well documented (Smail, J. et al, 1972). Laboratory studies have also been conducted to evaluate the effect of oil contamination on egg hatchability. Mallard duck (*Anas platyrhynchos*) eggs treated with 5 µl or more of Bunker C applied to the shells showed drastically reduced survival and hatching success reduced to 36% (Szaro, R.C., 1979; Green, J. and Trett, M.W., 1989). Ducklings which hatched from coated eggs, however, showed no significant weight differences from controls. Hatching success of brown pelican eggs (*Pelecanus occidentalis*) following a No. 6 oil spill was also reported to be significantly less than uncontaminated eggs (Green, J. and Trett, M.W., 1989). Quail eggs contaminated with Bunker C via maternal routes showed reduced egg production and reduced egg viability (NAP, 1985; Wootton, T.A. et al, 1979). Mallard ducks exposed to Bunker C by gizzard applications showed declining body weight with increasing exposure concentrations (Rocke, T.E. et al, 1984). Bunker C ingestion by these ducks also caused a significant increase in % mortality when exposed to *Pasteuiella multocida*, a pathogen. Based on this study, birds that survive initial coating of heavy fuel oil may have decreased resistance to disease or environmental perturbation.

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11.4. CONCLUSIONS/SUMMARY

The composition and resulting toxicity of heavy fuel oils varies depending on the amount and type of cutter stock used. Following accidental spillage of this oil, the lighter, more volatile components will be lost by evaporation, dissolution and biodegradation. The water-soluble fraction, which principally contains aromatic hydrocarbons and polar compounds, will be responsible for the acute toxicity effects on organisms. The remaining heavy fraction will become attached to the substrate or sequestered in the sediments. Little long-term impact has been observed in the supralittoral, littoral or pelagic zones following a spill. The tar-like residue will persist for many years, however, in the sediments with possible resuspension and continued impact on benthic organisms.

Table 8: Summary of aquatic toxicity data

Species	Material	Test Procedure	Effect --- Conc.	Reference
Fish				
Rainbow trout (*Oncorhynchus mykiss*)	Light fuel oil	WAF	96 hr. LL_{50} --- > 1000 mg/l	Eadsforth, 1997a
Rainbow trout (*Oncorhynchus mykiss*)	Heavy fuel oil	WAF	96 hr. LL_{50} --- 100-1000 mg/l	Eadsforth, 1997b
American shad (*Alosa sapidissma*)	No. 6 fuel oil	Static	48 hr. LC_{50} --- 2,417 mg/l	Tagatz, 1961
Sheepshead minnow (*Cyprinodon varieganus*)	Bunker C	WSF-1:9, 20 hr. mix, serial dilutions, LC_{50} based on ppm dissolved total hydrocarbons by IR	96 hr. LC_{50} --- 3.1 mg/l	Anderson et al, 1974a
Inland silversides (*Menidia berylina*)	Bunker C	WSF-1:9, 20 hr. mix, serial dilutions, LC_{50} based on ppm dissolved total hydrocarbons by IR	96 hr. LC_{50} --- 1.9 mg/l	Anderson et al, 1974a
Longnose killifish (*Fundulus similus*)	Bunker C	WSF-1:9, 20 hr. mix, serial dilutions, LC_{50} based on ppm dissolved total hydrocarbons by IR	96 hr. LC_{50} --- 1.7 mg/l	Anderson et al, 1974a
Atlantic silversides (*Menidia meridia*)	No. 6 fuel oil cutback with No. 2 fuel oil	Not given	EC_{50} --- 130 mg/l	Hollister et al, 1980
Bluegill sunfish (*Leopornis macrochirus*)	No. 6 fuel oil cutback with No. 2 fuel oil	Material heated, spread in container, water overlay	96 hr. LC_{50} --- >10,000 mg/l	Mobil, 1987

Table 8 (cont.)

Species	Material	Test Procedure	Effect --- Conc.	Reference
(Invertebrates)				
Polychaete (*Neanthes arenaceodentata*)	Bunker C	Not given	96 hr. LC_{50} --- 3.6 mg/l	Neff and Anderson, 1981
Polychaete (*Capitella capitata*)	Bunker C	Not given	96 hr. LC_{50} --- 0.9 mg/l	Neff and Anderson, 1981
Marine Copepod (*Acartia tonsa*)	No. 6 fuel oil cutback with No. 2 fuel oil	Not given	EC_{50} --- 5.1 mg/l	Hollister et al, 1980
Mysid Shrimp (*Mysidopsis almyra*)	Bunker C	WSF-1:9, 20 hr. mix, serial dilutions, LC_{50} based on ppm dissolved total hydrocarbons by IR	48 hr. LC_{50} --- 0..9 mg/l	Anderson et al, 1974a
Grass Shrimp (*Palaemonetes pugio*)	Bunker C	WSF-1:9, 20 hr. mix, serial dilutions, LC_{50} based on ppm dissolved total hydrocarbons by IR	96 hr. LC_{50} --- 2.6 mg/l	Anderson et al, 1974a
Brown Shrimp (*Penaeus aztecus*)	Bunker C	WSF-1:9, 20 hr. mix, serial dilutions, LC_{50} based on ppm dissolved total hydrocarbons by IR	96 hr. LC_{50} --- 1.9 mg/l	Anderson et al, 1974a

Table 8 (cont.)

Species	Material	Test Procedure	Effect --- CONCAWE	Reference
Grass shrimp (*Palaemonetes pugio*)	Bunker C	WSF-1:9, 20 hr. mix, serial dilutions, LC_{50} based on ppm dissolved total hydrocarbons by IR	96 hr.LC_{50} (21°F)--- 2.6 mg/l 96 hr.LC_{50} (21°F)--- 3.1 mg/l 96 hr.LC_{50} (21°F)--- 2.2 mg/l	Tatem et al, 1978
Daphnia magna	No. 6 fuel oil cutback with No. 2 fuel oil	WSF-1:8, 16 hr. mix, serial dilutions	48 hr. EC_{50} --->100% WSF	Giddings et al, 1980
Daphnia magna	No. 6 fuel oil cutback with No. 2 fuel oil	Material heated, spread as water overlay	48 hr. EC_{50} --->10,000 mg/l	Mobil, 1987
Daphnia magna	Light fuel oil	WAF	48 hr. EL_{50} --->1000 mg/l	Eadsforth, 1997a
Daphnia magna	Heavy fuel oil	WAF	48 hr. EL_{50} ---220-460 mg/l	Eadsforth, 1997b
American oyster (*Crassostrea virginica*)	Bunker C	mix oil and water 5 min., direct addition of test organisms	TL_{50} --- 6 days TL100 --- 13 days	Anderson, J.W., and Anderson, R.D., 1976
Quahog clam (*Mercenaria sp.*)	Bunker C	WSF-1:8, 12 hr. mix, serial dilutions, LC_{50} based on ppm dissolved total hydrocarbons by gravimetric analysis	48 hr. Embryo LC_{50} --- 1.0 mg/l 2 Day Larvae LC_{50} --- 3.2 mg/l 6 Day Larvae LC_{50} --- 1.8 mg/l 10 Day Larvae LC_{50} --- 1.6 mg/l	Byrne and Calder, 1977
Barnacle (*Balanus amphitrite niveus*)	Bunker C	WSF-1:8, 24 hr. mix, serial dilutions	1 hr; D_{50} --- 33% WSF	Donahue et al, 1977a
Stone crab (*Menippe mercenaria*)	Bunker C	WSF-1:8, 24 hr. mix, serial dilutions	54% survival --- 10% WSF (24 hrs.)	

Table 8 (cont.)

Species	Material	Test Procedure	Effect --- Conc.	Reference
Blue crab (*Calinectes sapidus*)	Bunker C	WSF-1:8, 24 hr. mix, serial dilutions	52% survival --- 50% WSF (24 hrs.)	Donahue et al, 1977b
Calico Crab (*Hepatus epheliticus*)	Bunker C	WSF-1:8, 24 hr. mix, serial dilutions	90% survival --- 20% WSF 20% survival --- 50% WSF (24 hrs.)	Donahue et al, 1977b
(Algae)				
Raphidocelis subcapitata	Light fuel oil	WAF --- OECD 201 --- GLP	72 hr EL_{50} SGR 100-300 mg/l 72 hr EL_{50} AUC 3-10 mg/l	Eadsforth, 1997a
Raphidocelis subcapitata	Heavy fuel oil	WAF --- OECD 201 --- GLP	72 hr EL_{50} SGR 30-100 mg/l 72 hr EL_{50} AUC 30-100 mg/l	Eadsforth, 1997b
Selenastrum capricornutum	No. 6 fuel oil	WSF-1:8, 16 hr. mix, serial dilutions,	No inhibition --- 100% WSF stimulation --- 0.1% WSF	Giddings et al, 1980
Microcystis aeruginosa	No. 6 fuel oil	WSF-1:8, 16 hr. mix, serial dilutions,	Inhibition --- 100% WSF stimulation --- 0.1% WSF	Giddings et al, 1980
Selenastrum capricornutum	No. 6 fuel oil	material heated, spread in Container, water overlay	96 hr. EC_{50} --- >5,000 mg/l	Mobil, 1987
Skeletonema costatum	Bunker C	Not given	EC_{50} --- 160 mg/l	Hollister et al, 1980

WAF: Water Accommodated Fraction
WSF: Water Soluble Fraction
SGR: Specific Growth Rate
AUC: Area Under Growth Curve
GLP: Good Laboratory Practice

Table 9: Effect of Bunker C on coral (Reimer A. A., 1975b)

Species	**Test Procedure**	**Time**	**Effect**
Pocillopora cf. darnicornis	1 min. direct oil exposure, depuration in clean water	13 days 16 days	70-84% tissue loss 100% tissue loss
Psammocora (Stephanaria) stellata	1 min. direct oil exposure, depuration in clean water	114 days	no change
Pavona gigantea	1 min. direct oil exposure, depuration in clean water	93 days 114 days	50% tissue loss 100% tissue loss
Porites furcata	1 min. direct oil exposure, depuration in clean water	114 days	100% tissue loss

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APPENDIX I

HEAVY FUEL OIL AND HEAVY FUEL OIL COMPONENTS

EINECS No.	CAS No.
265-045-2	64741-45-3

Residues (petroleum), atm. tower

A complex residuum from the atmospheric distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly greater than C20 and boiling above approximately 350 °C (662°F). This stream is likely to contain 5 wt % or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

265-058-3	64741-57-7

Gas oils (petroleum), heavy vacuum

A complex combination of hydrocarbons produced by the vacuum distillation of the residuum from atmospheric distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly in the range of C20 through C50 and boiling in the range of approximately 350°C to 600°C (662°F to 1112°F). This stream is likely to contain 5 wt. % or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

265-063-0	64741-61-3

Distillates (petroleum), heavy catalytic cracked

A complex combination of hydrocarbons produced by the distillation of products from a catalytic cracking process. It consists of hydrocarbons having carbon numbers predominantly in the range of C15 through C35 and boiling in the range of approximately 260 °C to 500°C (500°F to 932°F). This stream is likely to contain 5 wt. % or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

265-064-6	64741-62-4

Clarified oils (petroleum), catalytic cracked

A complex combination of hydrocarbons produced as the residual fraction from distillation of the products from a catalytic cracking process. It consists of hydrocarbons having carbon numbers predominantly greater than C20 and boiling above approximately 350°C (662°F). This stream is likely to contain 5 wt % or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

265-069-3   **64741-67-9**

Residues (petroleum), catalytic reformer fractionator

A complex combination of hydrocarbons produced as the residual fraction from distillation of the product from a catalytic reforming process. It consists of predominantly aromatic hydrocarbons having carbon numbers predominantly in the range of C10 through C25 and boiling in the range of approximately 160 °C to 400°C (320°F to 725°F). This stream is likely to contain 5 wt. % or more of 4- or 6-membered condensed ring aromatic hydrocarbons.

265-076-1   **64741-75-9**

Residues (petroleum), hydrocracked

A complex combination of hydrocarbons produced as the residual fraction from distillation of the products of a hydrocracking process. It consists of hydrocarbons having carbon numbers predominantly greater than C20 and boiling above approximately 350°C (662°F).

265-081-9   **64741-80-6**

Residues (petroleum), thermal cracked

A complex combination of hydrocarbons produced as the residual fraction from distillation of the product from a thermal cracking process. It consists predominantly of unsaturated hydrocarbons having carbon numbers predominantly greater than C20 and boiling above approximately 350°C (662°F). This stream is likely to contain 5 wt % or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

265-082-4   **64741-81-7**

Distillates (petroleum), heavy thermal cracked

A complex combination of hydrocarbons from the distillation of the products from a thermal cracking process. It consists predominantly of unsaturated hydrocarbons having carbon numbers predominantly in the range of C15 through C36 and boiling in the range of approximately 260°C to 480°C (500°F to 896°F). This stream is likely to contain 5 wt. % or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

265-162-9   **64742-59-2**

Gas oils (petroleum), hydrotreated vacuum

A complex combination of hydrocarbons obtained by treating a petroleum fraction with hydrogen in the presence of a catalyst. It consists of hydrocarbons having carbon numbers predominantly in the range of C13 through C50 and boiling in the range of approximately 230°C to 600°C (446°F to 1112°F). This stream is likely to contain 5 wt % or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

265-181-2   **64742-78-5**

Residues (petroleum), hydrodesulfurized atmospheric tower

A complex combination of hydrocarbons obtained by treating an atmospheric tower 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 C20 and boiling above approximately 350°C (662°F). This stream is likely to contain 5 wt % or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

265-189-6   **64742-86-5**

Gas oils (petroleum), hydrodesulfurized heavy vacuum

A complex combination of hydrocarbons obtained from a catalytic hydrodesulfurization process. It consists of hydrocarbons having carbon numbers predominantly in the range of C20 through C50 and boiling in the range of approximately 350°C to 600°C (662°F to 1112°F). This stream is likely to contain 5 wt. % or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

265-193-8   **64742-90-1**

Residues (petroleum), steam-cracked

A complex combination of hydrocarbons obtained as the residual fraction from the distillation of the products of a stream cracking process (including stream cracking to produce ethylene). It consists predominantly of unsaturated hydrocarbons having carbon numbers predominantly greater than C14 and boiling above approximately 260°C (500°F). This stream is likely to contain 5 wt. % or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

269-777-3   **68333-22-2**

Residues (petroleum), atmospheric

A complex residuum from atmospheric distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly greater than C11 and boiling above approximately 200°C (392°F). This stream is likely to contain 5 wt.% or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

269-782-0   **68333-26-6**

Clarified oils (petroleum), hydrodesulfurized catalytic cracked

A complex combination of hydrocarbons obtained by treating catalytic cracked clarified oil with hydrogen to convert organic sulfur to hydrogen sulfide which is removed. It consists of hydrocarbons having carbon numbers predominantly greater than C20 and boiling above approximately 350°C (662°F). This stream is likely to contain 5 wt. % or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

269-783-6   **68333-27-7**

Distillates (petroleum), hydrodesulfurized intermediate catalytic cracked

A complex combination of hydrocarbons obtained by treating intermediate catalytic cracked distillates with hydrogen to convert organic sulfur to hydrogen sulfide which is removed. It consists of hydrocarbons having carbon numbers predominantly in the range of C11 through C30 and boiling in the range of approximately 205°C to 450°C (401°F to 842°F). It contains a relatively large proportion of tricyclic aromatic hydrocarbons.

269-784-1   **68333-28-8**

Distillates (petroleum), hydrodesulfurized heavy catalytic cracked

A complex combination of hydrocarbons obtained by treatment of heavy catalytic cracked distillates with hydrogen to convert organic sulfur to hydrogen sulfide which is removed. It consists of hydrocarbons having carbon numbers predominantly in the range of C15 through C35 and boiling in the range of approximately 260°C to 500°C (506°F to 932°F). This stream is likely to contain 5 wt. % or more of 4- to 6- membered condensed ring aromatic hydrocarbons.

270-674-0   **68476-32-4**

Fuel oil, residues-straight-run gas oils, high-sulfur

270-675-6   **68476-33-5**

Fuel oil, residual

The liquid product from various refinery streams, usually residues. The composition is complex and varies with the source of the crude oil.

270-792-2   **68478-13-7**

Residues (petroleum), catalytic reformer fractionator residue distn.

A complex residuum from the distillation of catalytic reformer fractionator residue. It boils approximately above 399°C (750°F).

270-796-4   **68478-17-1**

Residues (petroleum), heavy coker gas oil and vacuum gas oil

A complex combination of hydrocarbons produced as the residual fraction from the distillation of heavy coker gas oil and vacuum gas oil. It predominantly consists of hydrocarbons having carbon numbers predominantly greater than C13 and boiling above approximately 230°C (446°F).

270-983-0   **68512-61-8**

Residues (petroleum), heavy coker and light vacuum

A complex combination of hydrocarbons produced as the residual fraction from the distillation of heavy coker gas oil and light vacuum gas oil. It consists predominantly of hydrocarbons having carbon numbers predominantly greater than C13 and boiling above approximately 230 °C(446°F).

270-984-6   **68512-62-9**

Residues (petroleum), light vacuum

A complex residuum from the vacuum distillation of the residuum from the atmospheric distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly greater than C13 and boiling above approximately 230°C (446°F).

271-013-9   **68513-69-9**

Residues (petroleum), steam-cracked light

A complex residuum from the distillation of the products from a steam-cracking process. It consists predominantly of aromatic and unsaturated hydrocarbons having carbon-numbers greater than C7 and boiling in the range of approximately 101°C to 555°C (214°F to 1030°F).

271-384-7   **68553-00-4**

Fuel oil, no. 6

A distillate oil having a minimum viscosity of 900 SUS at 37.7°C (100°F) to a maximum of 9000 SUS at 37.7°C (100°F).

271-763-7   **68607-30-7**

Residues (petroleum), topping plant, low-sulfur

A low-sulfur complex combination of hydrocarbons produced as the residual fraction from the topping plant distillation of crude oil. It is the residuum after the straight-run gasoline cut, kerosene cut and gas oil cut have been removed.

272-184-2   **68783-08-4**

Gas oils (petroleum), heavy atmospheric

A complex combination of hydrocarbons obtained by the distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly in the range of C7 through C35 and boiling in the range of approximately 121°C to 510°C (250°F to 950°F).

272-187-9   **68783-13-1**

Residues (petroleum), coker scrubber, condensed-ring-arom.-contg.

A very complex combination of hydrocarbons produced as the residual fraction from the distillation of vacuum residuum and the products from a thermal cracking process. It consists predominantly of hydrocarbons having carbon numbers predominantly greater than C20 and boiling above approximately 350°C (662°F). This stream is likely to contain 5 wt. % or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

273-263-4   **68955-27-1**

Distillates (petroleum), petroleum residues vacuum

A complex combination of hydrocarbons produced by the vacuum distillation of the residuum from the atmospheric distillation of crude oil.

273-272-3   **68955-36-2**

Residues (petroleum), steam-cracked, resinous

A complex residuum from the distillation of steam-cracked petroleum residues.

274-683-0   **70592-76-6**

Distillates (petroleum), intermediate vacuum

A complex combination of hydrocarbons produced by the vacuum distillation of the residuum from atmospheric distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly in the range of C14 through C42 and boiling in the range of approximately 250°C to 545°C (482°F to 1013°F) . This stream is likely to contain 5 wt.% or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

274-684-6   **70592-77-7**

Distillates (petroleum), light vacuum

A complex combination of hydrocarbons produced by the vacuum distillation of the residuum from atmospheric distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly in the range of C11 through C35 and boiling in the range of approximately 250°C to 545°C (482°F to 1013°F).

274-685-1   **70592-78-8**

Distillates (petroleum), vacuum

A complex combination of hydrocarbons produced by the vacuum distillation of the residuum from atmospheric distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly in the range of C15 through C50 and boiling in the range of approximately 270°C to 600°C (518°F to 1112°F). This stream is likely to contain 5 wt.% or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

285-555-9   **85117-03-9**

Gas oils (petroleum), hydrodesulfurized coker heavy vacuum

A complex combination of hydrocarbons obtained by hydrodesulfurization of heavy coker distillate stocks. It consists predominantly of hydrocarbons having carbon numbers predominantly in the range C18 to C44 and boiling in the range of approximately 304°C to 548°C (579°F to 1018°F). Likely to contain 5% or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

292-657-7   **90669-75-3**

Residues (petroleum), steam-cracked, distillates

A complex combination of hydrocarbons obtained during the production of refined petroleum tar by the distillation of stream cracked tar. It consists predominantly of aromatic and other hydrocarbons and organic sulfur compounds.

292-658-2   **90669-76-4**

Residues (petroleum), vacuum, light

A complex residuum from the vacuum distillation of the residuum from atmospheric distillation of crude oil. It consists predominantly of hydrocarbons having carbon numbers predominantly greater than C24 and boiling above approximately 390°C (734°F).

295-396-7   **92045-14-2**

Fuel oil, heavy, high-sulfur

A complex combination of hydrocarbons obtained by the distillation of crude petroleum. It consists predominantly of aliphatic, aromatic and cycloaliphatic hydrocarbons having carbon numbers predominantly higher than C25 and boiling above approximately 400°C (752°F).

295-511-0   **92061-97-7**

Residues (petroleum), catalytic cracking

A complex combination of hydrocarbons produced as the residual fraction from the distllation of the products from a catalytic cracking process. It consists predominantly of hydrocarbons having carbon numbers predominantly greater than C11 and boiling above approximately 200°C (392°F).

295-990-6   **92201-59-7**

Distillates (petroleum), intermediate catalytic cracked, thermally degraded

A complex combination of hydrocarbons produced by the distillation of products from a catalytic cracking process which has been used as a heat transfer fluid. It consists predominantly of hydrocarbons boiling in the range of approximately 220°C to 450°C (428°F to 842°F). This stream is likely to contain organic sulfur compounds.

298-754-0   **93821-66-0**

Residual oils (petroleum)

A complex combination of hydrocarbons, sulfur compounds and metal-containing organic compounds obtained as the residue from refinery fractionation cracking processes. It produces a finished oil with a viscosity above 2cSt. at 100°C.

308-733-0   **98219-64-8**

Residues, steam cracked, thermally treated

A complex combination of hydrocarbons obtained by the treatment and distillation of raw steam-cracked naphtha. It consists predominantly of unsaturated hydrocarbons boiling in the range above approximately 180°C (356°F).

309-863-0   **101316-57-8**

Distillates (petroleum), hydrodesulfurized full-range middle

A complex combination of hydrocarbons obtained by treating a petroleum stock with hydrogen. It consists predominantly of hydrocarbons having carbon numbers predominantly in the range of C9 through C25 and boiling in the range of approximately 150°C to 400°C (302°F to 752°F).