

FUEL OILS (HEATING OILS)

1. Chemical and Physical Data

1.1 Synonyms and trade names

Distillate fuel oils (light fuel oils)

Chemically-neutralized light distillate (CAS No. 64742-31-0); domestic fuel oil; domestic heating oil; fuel oil No. 1 (USA); fuel oil No. 2 (USA) (CAS No. 68476-30-2); furnace oil No. 1; furnace oil No. 2; heating oil; home heating oil; hydrotreated light distillate (CAS No. 64742-47-8); kerosene; kerosene, straight run [5]¹ (CAS No. 8008-20-6); kerosine; lamp oil; light heating oil; paraffin oil (UK); petroleum distillate; rotary burner fuel; stove oil

Residual fuel oils (heavy fuel oils)

Bunker C; bunker C fuel oil; bunker fuel oil; bunker oil; fuel oil lourde; fuel oil No. 4 (USA) (CAS No. 68476-31-3); fuel oil No. 5 (USA); fuel oil No. 6 (USA) (CAS No. 68553-00-4); fuel oil, residual (CAS No. 68476-33-5); industrial fuel oil; marine boiler fuels; power station fuel oil; residual fuel oil grade 4; residual fuel oil grade 5; residual fuel oil grade 6

1.2 Description

The fuel oils discussed in this monograph are used as burner fuel for domestic and industrial heating, and for raising steam for electricity generation and marine propulsion.

Because of the methods employed in their production, fuel oils fall into two broad classifications: distillates and residuals. The distillates consist of distilled process streams [5, 6, 6A, 7, 19, 24, 30]. The residual fuel oils are residues remaining after distillation [8, 21] or cracking [27, 31] and blends of these residues with distillates. In American Society for Testing and Materials (ASTM) Specification D 396 (Table 1), grades No. 1 and No. 2 are distillates and grades No. 4 to No. 6 are usually residual, although some heavy distillates [20, 26] may be sold as grade No. 4 (Hoffman, 1982).

¹See Table 2 and Figure 1 of the monograph on occupational exposures in petroleum refining

Table 1. Detailed requirements for fuel oils^a (ASTM specification D396^b)

Grade descriptions	No. 1	No. 2	No. 4 (Light)	No. 4	No. 5 (Light)	No. 5 (Heavy)	No. 6
Specific gravity, 15/15°C (°API)							
max	0.8499 (35 min)	0.8762 (30 min)		—	—	—	—
min	—	—	0.8762 ^c (30 max)	—	—	—	—
Flash-point, °C min	38	38	38	55	55	55	60
Pour-point, °C max	-18 ^d	-6 ^d	-6 ^d	-6 ^d	—	—	-e
Kinematic viscosity, mm ² /s (cSt) ^f							
At 38°C min	1.4	2.0 ^d	2.0	5.8	>26.4	>65	—
max	2.2	3.6	5.8	26.4 ^g	65 ^g	194 ^g	—
At 40°C min	1.3	1.9 ^d	—	5.5	>24.0	>58	—
max	2.1	3.4	—	24/0 ^g	(58) ^g	(168) ^g	—
At 100°C min	—	—	—	—	5.0	9.0	15.0
max	—	—	—	—	8.9 ^g	14.9 ^g	50.0
Saybolt viscosity ^f							
Universal at 38°C min	—	(32.6)	(32.6)	(45)	(>125)	(>300)	(>900)
max	—	(37.9)	(45)	(125)	(300)	(900)	(9000)
Furol at 50°C min	—	—	—	—	—	(23)	(>45)
max	—	—	—	—	—	(40)	(300)
Distillation temperature, °C							
10% point max	215	—	—	—	—	—	—
90% point min	—	282 ^d	—	—	—	—	—
max	288	338	—	—	—	—	—
Sulfur content, mass %, max	0.5	0.5 ^h	—	—	—	—	—
Corrosion copper strip, max	3	3	—	—	—	—	—

Table 1 (contd)

Grade descriptions	No. 1	No. 2	No. 4 (Light)	No. 4	No. 5 (Light)	No. 5 (Heavy)	No. 6
Ash, % mass, max	—	—	0.05	0.10	0.15	0.15	—
Carbon residue, 10% bottoms, mass %, max	0.15	0.35	—	—	—	—	—
Water and sediment, vol %, max	0.05	0.05	(0.50) ⁱ	(0.50) ⁱ	(1.00) ⁱ	(1.00) ⁱ	(2.00) ⁱ

^aFailure to meet any requirement of a given grade does not automatically place an oil in the next lower grade unless in fact it meets all requirements of the lower grade. No. 1, a distillate oil intended for vaporizing pot-type burners and other burners requiring this grade of fuel; No. 2, a distillate oil for general purpose heating for use in burners not requiring No. 1 fuel oil; No. 4 (light) and No. 4, preheating not usually required for handling or burning; No. 5 (light), preheating may be required depending on climate and equipment; No. 5 (heavy), preheating may be required for burning and, in cold climates, for handling; No. 6, preheating required for handling and burning

^bFrom American Society for Testing and Materials (1986)

^cThis limit guarantees a minimum heating value and also prevents misrepresentation and misapplication of this product as grade No. 2.

^dLower or higher pour-points may be specified whenever required by conditions of storage or use. When pour-point less than -18°C is specified, the minimum viscosity for grade No. 2 shall be 1.7 cSt (31.5 SUS) and the minimum 90% point shall be waived.

^eWhere low-sulfur fuel oil is required, a grade 6 fuel oil will be classified as low pour $+15^{\circ}\text{C}$ (max or high pour (no max)). Low pour fuel oil should be used unless all tanks and lines are heated.

^fViscosity values in parentheses are for information only and not necessarily limiting.

^gWhere low-sulfur fuel oil is required, fuel oil falling in the viscosity range of a lower numbered grade down to and including No. 4 may be supplied by agreement between purchaser and supplier. The viscosity range of the initial shipment shall be identified and advance notice shall be required when changing from one viscosity range to another. This notice shall be in sufficient time to permit the user to make the necessary adjustments.

^hIn countries outside the USA, other sulfur limits may apply.

ⁱThe amount of water by distillation plus the sediment by extraction shall not exceed the value shown in the table. For grade No. 6 fuel oil, the amount of sediment by extraction shall not exceed 0.50 wt %, and a deduction in quantity shall be made for all water and sediment in excess of 1.0 wt %.

(a) *Distillate fuel oils*

Specifications for both middle distillate heating fuels and transportation fuels are similar; as a consequence, it is often possible for refiners to satisfy the performance requirements of both applications with the same process stream or blend of process streams. The final products will have been treated (sweetened, dried, clay filtered, etc.) as required for a particular application, and may contain additives that are specific for the intended use, but they are otherwise virtually indistinguishable on the basis of their gross physical or chemical properties.

(i) *Fuel oil No. 1 (kerosene)*

The development of fuel oil No. 1 (kerosene) as a product can be traced back to Abraham Gesner, a Canadian doctor and geologist, who patented a distillation process for refining petroleum in 1854 (Anon., 1966). Gesner produced an improved illuminating oil which he called kerosene, derived from the Greek word *keros*, which means wax. The spelling is still widely used in industry, although the Chemical Abstracts preferred spelling is kerosine. Gesner first refined the oil from coal; thus, for many years, the product was widely known as 'coal oil', although the predominant source of the product changed from coal to petroleum crude oil. Kerosene remained the principal refined product of petroleum refiners for more than 50 years (Guthrie, 1960).

Fuel oil No. 1 is a light distillate intended for use in burners of the vaporizing type in which the oil is converted to a vapour by contact with a heated surface or by radiation. High volatility is necessary to ensure that evaporation proceeds with a minimum of residue.

Fuel oil No. 1 is generally a straight-run distillate with a boiling range consistent with the specifications shown in Table 1. (Refer to Table 2 and Figure 1 of the monograph on occupational exposures in petroleum refining for the processing history and generic definitions of refinery process streams.) Less often, it may consist of a blend of kerosene and light hydrocracked distillate and/or light catalytically cracked distillate [24]. Fuel oil No. 1 is not normally sweetened but usually contains an antioxidant additive.

(ii) *Fuel oil No. 2*

Fuel oil No. 2 is a heavier distillate than fuel oil No. 1. It is intended for use in atomizing-type burners, which spray the oil into a combustion chamber where the droplets burn while in suspension. This grade of oil is used in most home heating installations and in many medium-capacity commercial or industrial burners.

Fuel oil No. 2 is generally a blend of straight-run and catalytically cracked distillates. Typically, straight-run kerosene [5], straight-run middle distillate [6], hydrodesulfurized middle distillate [6A], straight-run gas oil [7], light catalytically cracked distillate [24], light vacuum distillate [19] and light thermally cracked distillate [30] are all candidates for blending into fuel oil No. 2. The streams and proportions used depend upon the nature of the refinery crude oil mix and the influence of the individual blend stocks on the specification properties set forth in ASTM D 396. Fuel oil No. 2 is generally dried by passage through salt driers and filtered to remove rust and dirt. Additives include antioxidants, dispersants and corrosion inhibitors. US distillate fuels contain a higher

proportion of cracked stocks and exhibit a narrower boiling range than those in most other parts of the world because of the greater degree of conversion carried out in order to maximize the yield of gasoline. The properties of a typical European distillate fuel oil for domestic or industrial use are given in Table 2.

Table 2. Typical properties of European fuel oil^a

Property	Distillate (domestic/industrial heating oil)	Residual		
		Light	Medium	Heavy
Kinematic viscosity at 50°C (cSt) – inland	2–7 (at 20°C)	20–30	30–180	180–600
– marine	–	20–30	30–180	180–600
Sulphur (wt %) – inland	0.5	<-----	0.3–5.0	----->
– marine	–	<-----	0.2–4.5	----->
Boiling range (°C)	160–400	–	–	–
Ash wt %	–	0.1	0.15	0.15
Water and sediment	–	<-----	1% max	----->

^aFrom CONCAWE (1985)

(b) Residual fuel oils

The most important specifications for residual fuel oils are the viscosity and sulfur content, although limits for flash-point, pour-point, water and sediment, and ash are included in ASTM D 396 (Table 1). Sulfur limits for the heavy fuels are controlled by federal, state and municipal regulation in the USA and consequently depend upon the location of use. For the heavier grades of industrial and bunker fuels, viscosity is of major importance. The imposition of viscosity limits ensures that adequate preheating facilities can be provided to permit transfer to the burner and atomization of the fuel. In addition, the maximal viscosity of fuel under storage conditions must be low enough to allow it to be pumped from the storage tank to the preheater. The properties of typical European residual fuel oils are shown in Table 2.

The principal manufacturing operation generally involves the addition of low viscosity blending stocks to high viscosity distillation residues in the proportions necessary to meet the viscosity specifications desired. The residues are typically atmospheric tower residue [8], vacuum residue [21] or thermally cracked residue [31]. Other residues, such as propane-precipitated bitumen, steam-cracked residue [34] (pyrolysis fuel oil) and solvent extracts of lubricant oils, are used infrequently. The blending stocks may be distillates or residues. Those frequently used are catalytically cracked clarified oil [27], heavy vacuum distillate [20] and heavy catalytically cracked distillate [26]. The specific refinery streams and the proportions in which the bottoms and the blending stock are combined depend upon market economics and on the viscosity specifications of the fuels being manufactured. In some

cases, the viscosity of the residue is such that no blending is required. In a refinery where the character of the crude oil and the nature of the processing units is such that both low and high sulfur residues are generated, these streams are generally segregated so that both low and high sulfur heavy fuels can be produced. Residual fuels blended from bottoms containing high levels of vanadium may require desalting in hot water to reduce the sodium content, since the presence of high levels of both sodium and vanadium results in undesirably high ash contents.

(i) *Fuel oil No. 4*

Fuel oil No. 4 is usually a 'light' residual, but it sometimes is, or contains, a heavy distillate. It is intended for use in burners equipped with devices that atomize oils of higher viscosity than domestic burners can handle. Its permissible viscosity range allows it to be pumped and atomized at relatively low storage temperatures. Consequently, in all but extremely cold weather, it requires no preheating for handling.

(ii) *Fuel oil No. 5*

Fuel oil No. 5 (light) is a residual fuel of intermediate viscosity for burners capable of handling fuel more viscous than fuel oil No. 4 without preheating. Fuel oil No. 5 (heavy) is a residual fuel more viscous than fuel oil No. 5 (light) and is intended for use in similar service. Preheating of fuel oil No. 5 may be necessary in some types of equipment for burning and in colder climates for handling.

(iii) *Fuel oil No. 6 (Bunker fuel)*

Fuel oil No. 6, sometimes referred to as 'bunker fuel' or 'bunker C', is a high viscosity oil used mostly as a boiler fuel and in commercial and industrial heating. It requires preheating in storage tanks to permit pumping and additional preheating at the burner to permit atomizing. The extra equipment and maintenance required to handle this fuel usually preclude its use in small installations.

1.3 Chemical composition and physical properties of technical products

Descriptions of the chemical composition and physical properties of fuel oils are available (Rossini *et al.*, 1953; Royal Dutch/Shell Group of Companies, 1983).

(a) *Distillate fuel oils*

Distillate fuel oils are complex mixtures of hydrocarbons that also contain minor amounts of sulfur-, nitrogen- and oxygen-containing molecules. They contain normal and branched alkanes, cycloalkanes (naphthenes), partially reduced aromatics and aromatics. If they have been blended in part with cracked stocks, they will also contain significant amounts of normal, branched and cyclic olefins, and aromatic olefins, such as styrenes and indenenes. Fuel oil No. 1 spans the carbon number range about C_9 – C_{16} ; fuel oil No. 2 spans the range about C_{11} – C_{20} . Although the complexity of the fuel oils precludes analysis of individual compounds, a number of studies of the composition of petroleum have provided

knowledge of the structures that predominate within a given broad hydrocarbon class and have shed some light on the relative abundance of isomers.

The normal alkanes occur in substantially all straight-run fractions with boiling ranges typical of those exhibited by distillate fuels, but their total concentration is dependent on the crude oil used. Branched alkanes also contribute significantly to the composition of distillates in this boiling range. Single-branched isomers predominate; the concentrations of double-branched isomers are an order of magnitude less than those with a single branch, and those of the triple-branched isomers two orders of magnitude lower. The cycloalkanes constitute a substantial portion of the saturated hydrocarbons in distillate fuels. Although the five- and six-membered-ring monocycloalkanes predominate in the lower-boiling fractions, bi- and tricycloalkanes have become increasingly important constituents in the 200–400°C boiling range. The majority of multi-ring cycloalkanes have five- and/or six-membered condensed ring systems. As a general rule in alkyl substitution, the derivatives of the parent ring system with alkyl substituents containing the smallest number of carbon atoms predominate over structures with longer chains.

The mononuclear aromatics consist largely of alkylbenzenes; however, the proportion of alkyl indanes and alkyl tetralins becomes larger as the average carbon number increases. Alkyl naphthalenes are the most abundant dinuclear aromatics. Although the condensed aromatic ring system predominates, small quantities of alkylbiphenyls, fluorenes and acenaphthenes are also present. As in the case of cycloalkanes, for which there are several possibilities for alkyl substitution, the predominant isomers are generally those containing substituents with the smallest number of carbon atoms. Phenanthrenes are the predominant trinuclear aromatic type. Generally, when three aromatic rings occur in the same molecule, they are usually condensed angularly rather than linearly. The boiling range of the distillate fuel oils precludes the presence of appreciable quantities of aromatics containing four or more condensed rings (Mair, 1964; Pancirov & Brown, 1975).

While these generalizations characterize the molecular structures that predominate within a broad hydrocarbon class, the proportions of each of the major classes can differ from one crude oil to another. Consequently, there may be appreciable variation in the hydrocarbon composition of distillate fuels; however, the differences are ordinarily not as large as might be anticipated because the specifications that must be met restrict the levels of several physical properties related to the composition. Detailed analyses of several samples of fuel oil No. 1 and fuel oil No. 2 are given in Table 3. Differences due to type of crude oil and process are discernible and are most evident in the distribution of saturated hydrocarbon types; nonetheless, the gross compositions are not remarkably divergent. The presence of catalytically cracked stocks does not result in the introduction of large quantities of olefins; even when the blended product contains 50% catalytic stock, the olefin content is below 10%. The use of catalytically cracked blend stocks generally results in fuels with some olefin content, reduced cycloalkane content and somewhat increased aromatic content, but which otherwise do not differ substantially from straight-run distillates.

Distillate fuels contain minor amounts of sulfur-, nitrogen- and oxygen-containing compounds, which in general are undesirable but can be tolerated at sufficiently low levels. In most refineries, processes for their reduction or removal are commonplace. The sulfur

Table 3. Detailed analyses of grades 1 and 2 distillate fuel oils^a

Hydrocarbon type, vol. %	Straight-run No. 1 furnace oils (two samples)		Hydrotreated No. 1 furnace oil	Straight-run No. 2 furnace oil	No. 2 furnace oil 10% cata- lytic stock	No. 2 furnace oil 50% cata- lytic stock
Paraffins (<i>n</i> - and <i>iso</i> -)	50.5	54.3	42.6	41.3	61.2	57.2
Monocycloparaffins	25.3	18.4	19.3	22.1	8.5	6.0
Bicycloparaffins	5.6	4.5	8.9	9.6	8.3	5.0
Tricycloparaffins	—	0.8	—	2.3	1.4	0.7
Total saturated hydrocarbons	81.4	78.0	70.9	75.3	79.4	68.9
Olefins	—	—	—	—	2.0	7.5
Alkylbenzenes	12.7	14.3	14.7	5.9	5.3	8.0
Indans/tetralins	2.9	3.8	7.5	4.1	4.3	5.4
Dinaphthenobenzenes/indenenes	—	0.9	—	1.8	1.3	1.0
Naphthalenes	3.0	2.6	6.9	8.2	5.8	6.8
Biphenyls/acenaphthenes	—	0.4	—	2.6	1.1	1.6
Fluorenes/acenaphthylenes	—	—	—	1.4	0.6	0.3
Phenanthrenes	—	—	—	0.7	0.2	0.5
Total aromatic hydrocarbons	18.6	29.1	22.0	24.7	18.6	23.6

^aProvided by the American Petroleum Institute

content of distillate fuels is limited to 0.5 wt % by ASTM D 396 and in Europe. The identities of a substantial number of these nonhydrocarbon molecules have been established. Nitrogen types include anilines, pyridines, quinolines, pyrroles, carbazoles, phenazines, benzonitriles and amides; sulfur occurs as thiols, sulfides, disulfides, thiophenes, thiaindanes, benzothiophenes and dibenzothiophenes, while oxygen-containing constituents are generally acids, ethers and ketones (Jewell *et al.*, 1965; Latham *et al.*, 1965; Thompson *et al.*, 1965; Green *et al.*, 1985).

The boiling range of kerosene fuel oil (fuel oil No. 1) generally precludes the occurrence of substantial quantities of polycyclic aromatic hydrocarbons. Fuel oil No. 2, consisting predominantly of atmospheric distillate streams, contains less than 5% three- to seven-ring polycyclic aromatic hydrocarbons (as measured by the dimethyl sulfoxide extraction method of the Institute of Petroleum). If high proportions of heavy atmospheric, vacuum or light cracked distillates are present, the level may be as high as 10% (CONCAWE, 1985). Some data on the concentrations of polycyclic aromatic hydrocarbons have been reported: Gräf and Winter (1968) found 0.029 ppm benzo[*a*]pyrene (see IARC, 1983, 1987a) in a heating oil; Pancirov and Brown (1975) determined the concentrations of a number of three- to five-ring aromatic hydrocarbons in two fuel oils — their data for fuel oil No. 2 are shown in Table 4. The total concentration of parent hydrocarbons containing four or more rings is just over 80 ppm; the concentration of benzo[*a*]pyrene is 0.6 ppm.

Table 4. Polynuclear aromatic compounds in one No. 2 fuel oil sample^a

Hydrocarbon	Molecular weight	Concentration (ppm)
Phenanthrene	178	429
2-Methylphenanthrene	192	7677
1-Methylphenanthrene	192	173
Fluoranthene	202	37
Pyrene	202	41
Benz[<i>a</i>]anthracene	228	1.2
Chrysene	228	2.2
Triphenylene	228	1.4
Benzo[<i>a</i>]pyrene	252	0.6
Benzo[<i>e</i>]pyrene	252	0.1

^aFrom Pancirov and Brown (1975)

As mentioned in section 1.2, distillate fuels often contain additives that serve as antioxidants, dispersants and corrosion inhibitors. Antioxidants may include hindered phenols, aminophenols and phenylenediamines. Dispersants may include various detergent amines, amidazolines, succinimides and amides; while corrosion inhibitors are typically long-chain alkyl carboxylates, sulfonates and amines.

(b) Residual fuel oils

Grades No. 4 to 6 fuel oils are commonly known as 'residual oils' since they are manufactured in whole or in part from distillation residues from refinery processing. Residual fuel oils are complex mixtures of relatively high molecular weight compounds and are difficult to characterize in detail. Since they are blended from fractions with boiling-points between 350 and 650°C, the molecular weights of the constituents can span the range from about 300 to over 1000. Molecular types include asphaltenes, polar aromatics, naphthalene aromatics, aromatics, saturated hydrocarbons and heteromolecules containing sulfur, oxygen, nitrogen and metals (Jewell *et al.*, 1974; Boduszynski *et al.*, 1981; CONCAWE, 1985). Fuels that have been prepared using catalytically cracked residues or heavy catalytically cracked distillates [26] contain some high molecular weight olefins and mixed aromatic olefins. In addition, they exhibit greater concentrations of condensed aromatics than do fuels prepared entirely from uncracked residues. Neff and Anderson (1981) characterized a No. 6 fuel oil (bunker fuel) in terms of the broad compositional categories shown in Table 5.

Table 5. Gross composition of a No. 6 fuel oil^a

Composition (wt %)		Elemental analysis (wt %)	
Saturates	21.1	Sulfur	1.46
Aromatics	34.2	Nitrogen	0.94
Polar aromatics	30.3	Nickel	89 (ppm)
Asphaltenes	14.4	Vanadium	73 (ppm)

^aFrom Neff and Anderson (1981)

Appreciable concentrations of polynuclear aromatic compounds are present in residual fuels because of the common practice of using both uncracked and cracked residues in their manufacture. Most blending stocks of residual fuel oils are likely to contain 5% or more of four- to six-ring condensed aromatic hydrocarbons. Pancirov and Brown (1975) reported the concentrations of a number of three- to five-ring condensed aromatics in a No. 6 fuel oil, as shown in Table 6. The identities and concentrations of the polynuclear aromatic compounds in a particular residual fuel depend on the nature and amount of the low viscosity blending stocks and the proportions of virgin and cracked residues. If the blending stocks are predominantly atmospheric [8] or vacuum residues [21], the concentration of three- to seven-ring aromatic hydrocarbons is likely to be of the order of 6–8%; if larger quantities of heavy catalytically cracked [26, 27] or steam-cracked [34] components are used, the level may approach 20% (CONCAWE, 1985). One of the blending stocks, catalytically cracked clarified oil [27], has been reported to contain 58% three- to five-ring aromatic hydrocarbons and 22% carbazoles and benzocarbazoles (Cruzan *et al.*, 1986).

Additives to improve the combustion of residual fuel oil, when used, are mostly based on oil-soluble compounds (e.g., naphthenates) of calcium, cerium, iron or manganese. Concentrations vary with fuel type but range typically from 50 to 300 ppm weight of the active metal

Table 6. Polynuclear aromatic compounds in one sample of No. 6 fuel oil^a

Hydrocarbon	Molecular weight	Concentration (ppm)
Phenanthrene	178	482
2-Methylphenanthrene	192	828
1-Methylphenanthrene	192	43
Fluoranthene	202	240
Pyrene	202	23
Benz[<i>a</i>]anthracene	228	90
Chrysene	228	196
Triphenylene	228	31
Benzo[<i>a</i>]pyrene	252	44
Benzo[<i>e</i>]pyrene	252	10
Perylene	252	22

^aFrom Pancirov and Brown (1975)

ingredient. They are usually added by the customer and are not incorporated into the fuel by the oil supplier. With increasing vanadium and sodium content of residual fuels, magnesium slurries suspended in gas oil or oil-soluble magnesium components are used to prevent corrosion at high temperatures. The amounts added depend on the vanadium concentration and are determined by a magnesium:vanadium weight ratio of up to 1.25:1.0 (CONCAWE, 1988).

2. Production, Use, Occurrence and Analysis

2.1 Production and use

Production and consumption of residual fuel oils in the USA and in the 24 countries of the Organisation for Economic Cooperation and Development (OECD) combined are presented in Table 7 for 1970–85 in five-year increments (International Energy Agency, 1987).

Comparative use of distillate and residual fuels in the USA for the period 1979–83 is shown in Table 8. The data for distillates include deliveries for transportation as well as for heating uses. Consumption of both distillate and residual fuel oils declined significantly: distillates by about 20% and residual fuels by almost 50%. About 80% of the decline in distillate demand is attributable to a pronounced reduction in the use of distillates in industrial and domestic heating systems.

Use of distillate fuel oils in the USA in 1979–83 is shown in Table 9. Heating utilization of the distillate grades (i.e., fuel oils No. 1 and No. 2) has declined substantially for all of the

Table 7. Production and consumption (in thousands of tonnes) of residual fuel oils in the USA and in countries of the Organisation for Economic Cooperation and Development (OECD) for 1970–85^a

Area	Production/ Consumption	1970	1975	1980	1985
USA	Production	38 665	88 009	101 945	57 109
	Consumption	67 083	47 978	51 372	27 396
OECD	Production	388 184	444 033	418 508	233 256
	Consumption	271 726	228 964	199 351	103 862

^aFrom International Energy Agency (1987)

Table 8. Deliveries of distillate and residual fuel oils by year in the USA (thousands of barrels)^a

Year	Distillate fuel oils	Residual fuel oils
1979	1 214 374	1 034 610
1980	1 086 709	937 466
1981	1 032 476	726 030
1982	974 864	626 510
1983	981 927	518 604

^aFrom US Department of Energy (1983)

Table 9. Deliveries of distillate fuel oils by use in the USA (thousands of barrels)^a

Year	All transportation	Heating				
		Residential	Commercial	Industrial	Farm	Oil company and electricity utility
1979	556 402	270 306	99 723	99 583	84 926	68 622
1980	531 497	227 361	92 136	86 089	73 615	56 017
1981	538 123	197 400	78 663	80 216	69 665	47 377
1982	517 360	180 760	75 699	71 340	68 453	41 616
1983 ^b	540 403	171 783	72 809	69 332	66 697	41 701

^aFrom US Department of Energy (1983) Estimates

^bEstimates

applications shown. Although fuel oil No. 1 is consumed in some residential and farm uses, it constitutes much less of the total supply of heating distillates than grade No. 2, which is the fuel most commonly used in residential heating installations and in many medium-capacity industrial burners. Residential heating constitutes the largest single nontransportation use of distillate fuels. While the intended use of these materials is as fuels, minor amounts may find their way into nonfuel uses, such as incorporation into drilling muds, herbicides and metal forming oils. The uses of kerosene range from its historical use as a lighting oil to oil for cooking and a source for fuel heating, both in furnaces and space heaters in homes and shops, and to industrial use as an aluminium roll oil.

Attempts were made to develop a carburettor that used kerosene in place of gasoline as a fuel during the early development of automobiles with an internal combustion engine. Although these efforts were abandoned, kerosene came into use as a light diesel fuel and is currently used as a diesel fuel No. 1 (see the monograph on diesel fuel), for instance, as a fuel for farm machinery. It has also had numerous other uses, e.g., as a degreasing solvent and weed killer and even in old-fashioned home remedies for treating snake bites, infections and as a deworming agent for animals and humans. It is still used in insecticides and other pesticides under regulated conditions.

Uses of residual fuel oils in the USA are shown in Table 10. Residual fuel oils are used by electric utilities, the maritime industry, industrial and commercial plants and factories, and in the petroleum industry in the production of process steam, space and water heating, and in applications such as pipeline pumping and gas compression. Electric power generation accounts for the largest percentage of US domestic consumption (~39% in 1983), followed by vessel bunkering, industrial commercial and oil company applications. Like distillates, residual fuel oils are sometimes used in nonfuel applications, such as road oils and in the manufacture of asphalt cements.

Table 10. Deliveries of residual fuel oils by use in the USA (thousands of barrels)^a

Year	Electric utility	Vessel bunkering	Industrial	Commercial	Oil company	All other
1979	486 636	190 543	198 759	82 729	51 062	24 881
1980	390 105	213 131	163 564	98 034	59 519	13 113
1981	325 486	188 632	117 024	67 035	51 870	11 981
1982	227 419	152 586	122 619	65 781	45 319	12 783
1983	204 328	136 290	89 573 ^b	46 743 ^b	32 820 ^b	8 940

^aFrom US Department of Energy (1983)

^bEstimates

2.2 Occurrence

(a) Occupational exposure

Potential occupational exposure to fuel oils (heating oils) has been associated with the following operations (CONCAWE, 1985): manually handled filling and discharge; tank dipping, pipeline and pump repairs, filter cleaning in refineries, distribution terminals and depots; tank inspection, cleaning and repair; servicing, testing and maintaining heating systems and equipment using heating oil; routine sampling and laboratory handling of fuel oils; and practices in which heating oils are used as cleaning agents or solvents.

Worker exposure to hydrocarbons was measured during the cleaning of ten tanks containing different types of heating oil in Sweden. The concentration of total hydrocarbons (personal sampling) was found to range from 240 mg/m³ (time-weighted average (TWA) during 55 min) to 1615 mg/m³ (TWA during 45 min). Hydrocarbon concentrations were higher in the cleaning of heavy oil industrial tanks than in the cleaning of home fuel oil tanks. The difference was ascribed to vaporization of heavy oil due to its handling in the heated state (Ahlström *et al.*, 1986).

Similar results were obtained in another Swedish study on tank cleaners with short-term samples ranging from 89 mg/m³ (tank size, 3 m³) to 1032 mg/m³ (tank size, 150 m³) for total hydrocarbons. Benzene (see IARC, 1982, 1987b) concentrations ranged from 4 to 8 mg/m³. Vaporized domestic oil was found to consist of about 50% linear or branched alkanes (carbon numbers 6–14), 20% cyclopentanes and cyclohexanes and about 30% alkylbenzenes (Lillienberg, 1986; Lillienberg *et al.*, 1987).

Readings of total hydrocarbon levels taken in one emptied light-oil tank ranged from 100–300 ppm (Högstedt *et al.*, 1981). Oil tank cleaners were described as spraying white spirit and xylene onto the walls of tanks that had contained heavy oils.

The use of residual fuel oils as heating oils may result in the evolution of hydrogen sulfide gas when they are manipulated while hot (CONCAWE, 1985).

(b) Environmental occurrence

Table 11 lists some accidental releases of fuel oil that have been reported in the recent past.

2.3 Analysis

Since fuel oils are composed of a complex mixture of hydrocarbons, there are few methods for the environmental analysis of 'fuel oils' as an entity, but many methods are reported for the analysis of their component hydrocarbons. These methods are used to identify or 'fingerprint' the origin of a specific fuel oil sample on the basis of the proportions of its component hydrocarbons.

A method for the mass measurement of hydrocarbons has been applied to monitoring fuel oil vapour. It involves the collection of vapours in graphite tubes, their extraction and subsequent measurement with an infrared spectrophotometer (Ahlström *et al.*, 1986).

Table 11. Recent, selected, large accidental releases of fuel oil (heating oil)

Place	Date	Type	Quantity	Reference
West Falmouth, MA, USA	September 1969	Fuel oil No. 2 from grounding of barge, <i>Florida</i>	650 000– 700 000 l	Blumer & Sass (1972); Sanders <i>et al.</i> (1980)
Chedabucto Bay, Nova Scotia, Canada	February 1970	Bunker C fuel oil from grounding of tanker, <i>Arrow</i>	108 000 barrels (1.75 million l)	Levy (1971); Keizer <i>et al.</i> (1978)
Brittany coast, France	March 1980	Bunker C fuel oil from wreck of tanker, <i>Tanio</i>	8100 tonnes	Berne & Bodennec (1984)
Yaquina Bay, OR, USA	November 1983	Bunker C fuel oil and diesel fuel from wreck of tanker, <i>Blue Magpie</i>	284 000 l	Kemp <i>et al.</i> (1986)
Stockholm, Sweden	October 1977	Fuel oil No. 5 from grounding of tanker, <i>Tsesis</i>	>1000 tonnes	Johansson <i>et al.</i> (1980)
Searsport, ME, USA	March–June 1971	Storage facility spill of fuel oil No. 2 mixed with JP-5 jet fuel	>14 tonnes	Dow <i>et al.</i> (1975)
Floreffe, PA, USA	December 1987	Rupture of fuel oil No. 2 storage tank ^a	3 million gallons (11.4 million l)	MacKerron & Kiesche (1988)

^aSee also the monograph on diesel fuel

Methods based on charcoal adsorption, carbon disulfide desorption and analysis by gas chromatography with various calibration standards have been reported and compared with the infrared spectrophotometric method (Lillienberg, 1986; Lillienberg *et al.*, 1987).

3. Biological Data Relevant to the Evaluation of Carcinogenic Risk to Humans

3.1 Carcinogenicity studies in animals

Studies on the carcinogenicity in experimental animals of straight-run kerosene [5], light [24] and heavy [26] catalytically cracked distillates, light [19] and heavy [20] vacuum distillates, catalytically cracked clarified oils [27], thermally cracked residues [31] and steam-cracked residues [34], which are components of fuel oils, are described in the monograph on occupational exposures in petroleum refining.

Skin application¹

Mouse: Groups of 19–40 C3H mice [sex and age unspecified] received twice weekly [duration unspecified] skin applications [not otherwise specified] of 20 or 50 mg of blended fuel oils obtained by adding different amounts of residue [31] (>371°C) from thermal cracking of catalytically cracked clarified oil [the material tested was essentially thermally cracked residue [31]; the feed stream [27] is of secondary importance] to either a cracked bunker fuel (base stock A) or a West Texas uncracked residue [8 or 21] (base stock B). The benzo[*a*]pyrene content of the two blends and the incidences of skin tumours are given in Table 12. Cracked bunker fuel produced malignant and benign skin tumours at both dose levels. The addition of various amounts of cracked residue resulted in an increase in tumour frequency and a decrease in latency (Bingham *et al.*, 1980). [The Working Group noted that the original work was carried out by another investigator (Horton, 1957) in the same laboratory.]

Groups of 25 male and 25 female C3H/Bd_f mice, six to eight weeks old, received thrice weekly skin applications on a 1-cm² clipped dorsal area of 50 µl undiluted, 1:1 diluted or 1:3 diluted fuel oil No. 2 (American Petroleum Institute No. 975) in acetone [duration unspecified]. Animals were killed two weeks after tumour appearance. Groups of 25 male and 25 females received thrice weekly applications of 50 µg, 25 µg or 12.5 µg benzo[*a*]pyrene dissolved in 50 µl acetone and served as positive controls. Further groups of 50 males and 50 females received 50 µl acetone thrice weekly or no treatment and served as negative controls. The fuel oil sample contained 0.04 µg/g benzo[*a*]pyrene, 0.07 µg/g five- to six-ring polycyclic aromatic hydrocarbons (1.2 wt % polyaromatic hydrocarbons). Of 150 mice treated with fuel oil No. 2, 15 developed 17 carcinomas and two papillomas of the skin. No skin tumour was observed in the acetone-treated or untreated control groups, whereas benzo[*a*]pyrene induced tumours in nearly all mice (Witschi *et al.*, 1987). [The Working Group noted that the exact distribution of tumours among the various treated groups was not reported.]

3.2 Other relevant data

(a) *Experimental systems*

Absorption, distribution, excretion and metabolism

(i) *Fuel oil No. 1 (Kerosene)*

Aromatic hydrocarbons were found in the blood of rats following intragastric administration of kerosene for domestic use (Gerarde, 1959, 1964).

Baboons were administered kerosene [unspecified] (15 ml/kg bw) labelled with ³H-toluene or ¹⁴C-hexadecane by nasogastric intubation after a tracheotomy had been performed. After 6 h of exposure, ³H-toluene appeared to have been absorbed and taken up by most tissues to a greater extent than ¹⁴C-hexadecane (Mann *et al.*, 1977).

¹The Working Group was aware of skin-painting studies in progress in mice using fuel oil No. 2 based on straight-run middle distillate [6] (three samples) or light catalytically cracked distillate [24] (three samples) (IARC, 1986).

Table 12. Incidences of skin tumours in C3H mice following application of blended fuel oils^a

Base blending stock ^b	Cracked residue added (%)	Benzo[a]-pyrene content (%)	Dose (mg)	No. of mice	Final effective number ^c	No. of mice developing tumours		Average time to appearance of papillomas	
						Malignant	Benign	Weeks	SD
A	0	0.01	20	19	17	1	1	—	
			50	20	17	3	7	58.8	4.7
B	0	0	20	40	23	0	1	—	
A	5	0.05	20	30	27	15	8	41.5	3.6
			50	30	27	13	8	28.3	3.3
B	5	0.04	20	40	31	9	11	49.1	5.5
			50	48	27	9	9	36.9	3.3
A	10	0.08	20	30	26	19	7	40.4	3.2
			50	30	25	22	3	32.2	2.5
B	10	0.075	20	40	35	22	13	40.5	1.9
			50	30	30	9	18	26.7	1.6
A	20	0.16	20	25	23	12	9	25.2	2.8
B	20	0.15	20	29	28	11	16	23.4	1.7

^aFrom Bingham *et al.* (1980)

^bA, cracked bunker fuel; B, West Texas uncracked residue

^cNumber alive at the time of appearance of the median tumour plus the number of tumour-bearing mice that died earlier

(ii) *Fuel oil No. 2*

The accumulation and release of petroleum hydrocarbons by aquatic organisms, including selected data on fuel oil No. 2, have been reviewed (Lee, 1977; Neff & Anderson, 1981). Fuel oil No. 2 has been shown to be metabolized to conjugates of several two- and three-ring aromatic hydrocarbons in fish (Krahn & Malins, 1982; Hellou & Payne, 1987).

Toxic effects

(i) *Fuel oil No. 1 (kerosene)*

The oral LD₅₀ of one brand of kerosene was 28 ml/kg bw in rabbits and 20 ml/kg bw in guinea-pigs, while 28 ml/kg bw killed four of 15 rats (Deichmann *et al.*, 1944). The LD₅₀ for kerosene administered by the intratracheal route was approximately 1 ml/kg bw (Gerarde, 1959).

Air saturated at 25°C with deodorized kerosene vapours (55.2% paraffins, 40.9% naphthenes, 3.9% aromatics; 0.10 mg/l (14 ppm)) did not induce death in rats, dogs or cats following an 8-h inhalation period (Carpenter *et al.*, 1976).

In tracheotomized monkeys killed 6–8 h after administration of 45 ml/kg bw kerosene [presumably for domestic use] via a nasogastric tube, macroscopic and microscopic examination showed heavy oedematous lungs with patchy haemorrhagic areas. Similar results were observed in animals receiving 1.0 ml kerosene intravenously or 0.2 ml endotracheally (Wolfsdorf & Kundig, 1972).

The lungs of rabbits administered 25 ml/kg bw kerosene [presumably for domestic use] by stomach tube showed slight congestion and focal atelectasis but no evidence of pneumonia or bronchitis when the animals were killed seven days after dosing (Richardson & Pratt-Thomas, 1951).

Both an intravenous dose of 0.50 ml/kg bw kerosene [presumably for domestic use] and an intratracheal dose of 1.0 ml/kg bw were fatal to dogs after 8 h and 10 min, respectively. Dogs administered kerosene by stomach tube at doses of 2–30 ml/kg bw survived. In animals that were sacrificed and autopsied one to 18 days after receiving the oil, severe lung damage was seen only in animals that had vomited (Richardson & Pratt-Thomas, 1951).

Levels of haem biosynthesis enzymes (δ -aminolaevulinic acid synthetase and dehydratase) were decreased in the liver of Wistar rats 3 and 20 h after intraperitoneal administration of commercial kerosene (1.0 ml/kg bw), whereas levels of haem oxygenase (involved in haem degradation) remained unchanged (Rao & Pandya, 1980).

Rats exposed to deodorized kerosene mists at concentrations of 75 and 300 mg/m³ for 14 days developed liver steatosis characterized by an increase in free fatty acids, phospholipids and cholesterol esters and decreases in triglycerides. Various serum enzyme levels were also elevated (Starek & Kamiński, 1982).

When rats were given repeated subcutaneous administrations of commercial kerosene (0.5 ml/kg bw) on six days a week for 35 days, the weights of the liver, spleen and peripheral lymph nodes were increased and there were corresponding increases in the DNA, RNA, protein and lipid contents of liver and spleen. Histopathological effects were observed in a variety of tissues, while lymphocyte counts were lowered and neutrophil counts elevated.

The activity of liver alkaline phosphatase increased and that of benzo[*a*]pyrene hydroxylase decreased. Serum cholinesterase and carboxylesterase activities and albumin levels were reduced, while serum alkaline phosphatase activity was greatly enhanced (Rao *et al.*, 1984).

A group of 12 male and female guinea-pigs was exposed to kerosene [product obtained directly from a refinery] aerosols (ranging from 20.4 to 34 mg aerosol/l air) for 15 min daily over 21 consecutive days. Ten animals were kept in atmospheric air. Increased numbers of macrophages, neutrophils, eosinophils and lymphocytes were found in the pulmonary washings of treated animals (Noa *et al.*, 1985). Severe alterations of the ciliated epithelium of the trachea were also observed in five male guinea-pigs given a mean concentration of 32.5 mg/l (Noa & Sanabria, 1984). In 23 male guinea-pigs exposed to 20.4–34 mg/l, aortic plaques developed, with fibrous tissue, collagen and elastic fibres, and smooth-muscle cells resembling those seen in atherosclerosis (Noa & Illnait, 1987).

(ii) *Fuel oil No. 2*

The oral LD₅₀s of three No. 2 home heating oils in rats were 12.0, 15.7 and 17.5 g/kg bw. No mortality was induced in rabbits painted on the skin with the oils at 5 g/kg bw (Beck *et al.*, 1984).

The toxic effects of fuel oil No. 2 in birds and aquatic organisms have been reviewed (Rice *et al.*, 1977; Holmes *et al.*, 1978; Szaro *et al.*, 1981; Wells & Percy, 1985).

(iii) *Bunker fuel*

No adverse effect was observed in sheep fed about 100 g (10% in hay) bunker fuel per day for up to ten days (MacIntyre, 1970).

Effects on reproduction and prenatal toxicity

As reported in a review of teratology studies in rats exposed to different fuels by inhalation, exposure of animals on days 6–15 of gestation for 6 h per day to 100 and 365 ppm kerosene [unspecified] or to 85 and 410 ppm fuel oil No. 2 resulted in no teratogenic effect (Schreiner, 1984). [The Working Group noted that details were not reported.]

Several studies have shown pronounced effects of fuel oil No. 2 on the reproductive capacity of birds after application on the shell surface (decreased hatchability, deformed bills, dead embryos; Albers & Szaro, 1978; Coon *et al.*, 1979; White *et al.*, 1979; Albers & Heinz, 1983). Studies in chick embryos with fractionated fuel oil No. 2 indicated that toxicity was associated primarily with the two- to three-ring aromatic fraction (Ellenton, 1982). Bunker fuel also reduced duck egg hatchability (Szaro, 1979). [The Working Group noted that the avian system is a sensitive model for embryotoxic effects; results should be interpreted with caution with respect to possible effects in mammalian systems.]

Genetic and related effects

(i) *Fuel oil No. 1 (kerosene)*

Kerosene (boiling range, 177–271°C; 18% aromatics) was not mutagenic to *Salmonella typhimurium* TA98 or TA100 in the presence or absence of an exogenous metabolic system

from rat liver, using the plate incorporation (0.001–5 $\mu\text{l}/\text{plate}$) or suspension (6.25–50 $\mu\text{l}/\text{ml}$) methods. It did not induce forward mutations in mouse lymphoma L5178Y TK^{+/–} cells in the presence or absence of an exogenous metabolic system from rat or mouse liver. Kerosene did not induce chromosomal aberrations in the bone marrow of Sprague-Dawley rats killed 6 and 48 h after a single intraperitoneal injection of 0.04–0.4 ml/rat or after repeated daily intraperitoneal injections of 0.02–0.18 ml/rat for five days (Conaway *et al.*, 1984).

(ii) *Fuel oil No. 2*

Fuel oil No. 2 gave borderline positive results for mutagenicity in *S. typhimurium* TA98 and TA100 both in the presence and absence of an exogenous metabolic system from rat liver, using the plate incorporation method (0.26–42 mg/plate), while it was clearly mutagenic to mouse lymphoma L5178Y TK^{+/–} cells in forward mutation assays at a concentration of 1.2 $\mu\text{l}/\text{ml}$ in the absence of an exogenous metabolic system, giving a mutation frequency 17.1 times that in solvent control cultures (Conaway *et al.*, 1984).

Of three fractions of fuel oil No. 2 tested in *S. typhimurium* TA1535, TA1537, TA1538, TA98 and TA100, only the four- to seven-ring polycyclic aromatic hydrocarbon fraction induced a dose-dependent increase in the number of revertants in strain TA100 in the presence of an exogenous metabolic system from Aroclor 1254-induced rat liver. The same fraction and the one- to three-ring aromatic hydrocarbon fraction caused dose-dependent increases in the frequency of sister chromatid exchange, but not of chromosomal aberrations, in Chinese hamster ovary cells in the presence of an exogenous metabolic system from Aroclor 1254-induced rat liver (Ellenton & Hallett, 1981).

As reported in an abstract, home heating oil [not otherwise specified] induced transformed foci in both BALBc/3T3 and C3H/10T1/2 cells (Butala *et al.*, 1985).

Fuel oil No. 2 induced chromosomal aberrations in the bone marrow of Sprague-Dawley rats administered 0.125–1.25 g/kg bw per day by gavage for five successive days (Conaway *et al.*, 1984).

(iii) *Residual fuel oils*

Bunker fuel was not mutagenic to *S. typhimurium* TA1535, TA1538, TA98 or TA100 either in the presence or absence of an exogenous metabolic system from Aroclor 1254-induced rat liver (Vandermeulen *et al.*, 1985), and did not induce forward mutation (streptomycin resistance) in *Chlamydomonas reinhardtii* (Vandermeulen & Lee, 1986). As reported in an abstract, dual-purpose and residual fuel oil were not active in *S. typhimurium* in the presence or absence of an exogenous metabolic system from Aroclor 1254-induced rat liver (Farrow *et al.*, 1983).

B-class heavy oil (containing many polycyclic aromatic hydrocarbons and basic nitrogen-containing chemicals, such as aza-arenes) induced an increase in the frequency of chromosomal aberrations in cultured Chinese hamster lung cells (12% versus <5% in controls) at a concentration of 2.0 mg/ml in the presence of an exogenous metabolic system from rat liver. A fraction separated by liquid-liquid extraction, in which the basic nitrogen-containing polycyclic hydrocarbons were included, gave clearly positive results and was

more active (e.g., 17% at 0.48 mg/ml; 24.0% at 0.25 mg/ml for the same fraction of another lot of B class heavy oil) than the unfractionated oil. Other similarly extracted fractions, containing high molecular weight hexane-insoluble ingredients or *n*-paraffin, *iso*-paraffin, polycyclic hydrocarbons and sulfur-containing compounds, or neutral or weakly basic nitrogen-containing compounds, did not induce chromosomal aberrations in cultured Chinese hamster lung cells even in the presence of an exogenous metabolic system (Matsuoka *et al.*, 1982).

As reported in an abstract, dual-purpose and residual fuel oils did not induce sister chromatid exchange in cultured Chinese hamster ovary cells nor mutations in cultured mouse lymphoma L5178Y TK^{+/-} cells, in the presence or absence of an exogenous metabolic system from Aroclor 1254-induced rat liver (Farrow *et al.*, 1983).

(b) Humans

Absorption, distribution, excretion and metabolism

No adequate data were available to the Working Group.

Toxic effects

Series of tens to hundreds of cases of accidental ingestion of kerosene in children have been reported from Australia (Isbister, 1963), Barbados (St John, 1982), Denmark (Brunner *et al.*, 1964), India (Saksena, 1969), Indonesia (Aldy *et al.*, 1978), Iraq (Nouri & Al-Rahim, 1970), Kuwait (Majeed *et al.*, 1981), the USA (Nunn & Martin, 1934; Heacock, 1949), Zaire (Muganga *et al.*, 1986), Zimbabwe (Baldachin & Melmed, 1964) and other countries. Kerosene poisoning is a common childhood poisoning in some parts of the world; similar effects can occur in adults (Vidal & Ferrando, 1974).

Childhood kerosene poisoning (Nunn & Martin, 1934; Heacock, 1949; Isbister, 1963; Brünner *et al.*, 1964) usually occurs in children from one to three years old, most often in boys. Most cases are mild. In those more severely affected, there is initial coughing and involuntary deep respiration, followed by accelerated, rattling breathing, tachycardia and cyanosis, frequently associated with spontaneous vomiting, nausea and abdominal pain. Bronchopneumonia frequently occurs. Chest X-ray findings include multiple, small, cloudy lung infiltrations, which may coalesce to form lobular or lobar infiltrations, mostly in the lung bases. Bilateral perihilar vascular markings may also be seen. The pneumonia and X-ray changes usually resolve within several days. Complications include pleural effusion (Scott, 1944; Tal *et al.*, 1984), pneumatocele (Tal *et al.*, 1984), oedema (Lesser *et al.*, 1943) and, more rarely, mediastinal and soft-tissue emphysema (Scott, 1944; Marandian *et al.*, 1981). Central nervous system depression is seen in a minority of patients, which may progress to coma and convulsions (Nouri & Al-Rahim, 1970; Aldy *et al.*, 1978). Death occurs in up to 10% of reported cases. Individuals who die usually have rapid onset of shock and pulmonary changes, and may have convulsions. Autopsy shows generalized haemorrhagic oedema of the lungs (Baldachin & Melmed, 1964) and may show cellular degeneration in the liver (Nunn & Martin, 1934).

Subclinical small airway abnormalities and abnormal chest radiographs (residual bullae or increased markings) can be seen ten years after childhood kerosene pneumonitis; their presence is related to the severity of the acute primary pneumonia (Tal *et al.*, 1984).

Indonesian kerosene retailers who were frequently in contact with kerosene developed nocturnal itching, reddening, peeling and chapping of the skin (Suma'mur & Wenas, 1978). Irritant dermatitis has been seen in children following contact with kerosene-soaked clothing (Tagami & Ogino, 1973).

In skin patch tests of kerosene products with boiling ranges of 177–316°C, irritant reactions, sometimes of severe degree, were produced in most individuals; irritation was correlated with kerosene content. Kerosene of paraffinic origin was less irritating than that of naphthenic origin within the same boiling range (Klauder & Brill, 1947; Tagami & Ogino, 1973).

Effects on reproduction and prenatal toxicity

No data were available to the Working Group.

Genetic and related effects

A group of 16 tank cleaners were studied for cytogenetic changes; a subgroup of men who had cleaned light and heavy oil tanks was also included. Micronuclei in bone-marrow cells and chromosomal aberrations in peripheral blood lymphocytes were reported to be significantly more prevalent in the whole group than in the control group (Högstedt *et al.*, 1981). [The Working Group noted that the results were not reported separately for the different subgroups of cleaners and that the workers would have been subjected to mixed exposures.]

3.3 Epidemiological studies and case reports of carcinogenicity to humans

(a) Cohort studies

Tsuchiya (1965) conducted a large historical cohort study of some 400 000 (1 200 000 person-years) Japanese workers during the period 1957–59. Information on both exposure and disease was obtained from questionnaires distributed to health supervisors of 200 companies each employing over 1000 persons; 100% of the forms were returned. Exposure was defined either as the type of chemicals to which the worker had been exposed, listed by the health supervisor, or as the type of industry in which he was employed. No measurement of level or length of exposure was obtained. During the three-year period, 808 cancer cases were identified, 492 of which resulted in death, among workers aged 20–59 years. An excess of lung cancer (55 deaths and newly-diagnosed cases) was observed among workers described as having been exposed to kerosene, diesel oil, crude petroleum and mineral oil [estimated odds ratio, 2.7; 95% confidence interval (CI), 1.4–5.3] when considered as a group. [The Working Group noted the poor statistical analysis and the poor handling of the limited information on smoking.]

Okubo and Tsuchiya (1974) conducted a large cohort study that covered a population of about 1 200 000 employees at 515 factories in Japan. Information on exposure and on cancer

deaths was obtained from questionnaires distributed to health supervisors in each factory. Exposure was assessed by industry, occupation, duration of employment and possible exposure to chemical or physical agents. During the period 1966–68, 1140 cancer deaths were identified. After controlling for age and sex, an excess of stomach cancer was observed among workers possibly exposed to kerosene, machine oil or grease. Leukaemia was reported to have occurred in excess in industries where kerosene, paraffin oil or petroleum combustibles were reported as having been used or produced.

[The Working Group noted that the results of these two studies are difficult to interpret due to the very general assessment of exposure and to the lack of information on expected numbers and on confounding variables.]

(b) *Case-control studies*

Using data from the Third National Cancer Survey, the National Occupational Hazard Survey and the National Health and Nutrition Examination Survey to investigate occupational health problems, Spiegelman and Wegman (1985) conducted a case-control study of 343 men diagnosed as having a colorectal cancer between 1969 and 1971 in seven US metropolitan areas and two states. Controls were 626 men with cancers other than of the digestive system, respiratory tract, urinary tract, bone, skin, mouth or pharynx or leukaemia. Exposure to 11 occupational carcinogens was assessed from occupations and industries reported to the Third National Cancer Survey. In order to control for diet as a potential confounder, a nutritional score was calculated for each subject on the basis of data from the National Health and Nutrition Examination Survey. Using logistic regression analysis, the authors observed an increased odds ratio for colorectal cancer associated with exposure to solvents (odds ratio, 1.6; 95% CI, 1.1–2.3; $p = 0.01$) and to fuel oil (odds ratio, 1.5; 1.1–2.0; $p = 0.01$), controlling for age, weight, race and diet. The increases were slightly higher for colon cancer. There was a trend with increasing exposure to solvents but not to fuel oil. [The Working Group noted that exposure to neither ‘fuel oil’ nor ‘solvent’ was defined, but the two were highly correlated.]

In a large case-control study of cancer at many sites in Montréal, Canada, which is described in detail in the monograph on gasoline (p. 185; Siematycki *et al.*, 1987), an association was observed between exposure to kerosene and stomach cancer (adjusted odds ratio, 1.7; 90% CI, 1.2–2.5) and between exposure to heating oil and rectal cancer (adjusted odds ratio, 1.4; 0.7–2.7); with ‘substantial’ exposure to heating oil, the odds ratio for rectal cancer was 2.6 (1.2–5.5). There was also a significant association between exposure to heating oil and oat-cell cancer of the lung (odds ratio, 1.7; 1.2–3.4). The authors noted that the association between kerosene and stomach cancer was entirely attributable to a stomach cancer risk among forestry workers.

Three case-control studies were carried out to investigate the high incidence of lung cancer in women in Hong Kong in relation to use of kerosene cooking stoves. In comparing the cooking habits of 44 women with histologically demonstrated lung cancer with those of 314 families interviewed at random in Hong Kong, Leung (1977) observed that a higher proportion of cases (91%) had used kerosene cooking stoves than controls (36%). The

authors concluded that both exposure to kerosene stoves and cigarette smoking were strongly associated with lung cancer in women in Hong Kong.

In a similar study in which 189 hospitalized women with a histologically confirmed diagnosis of bronchial cancer were compared with 189 control patients from the orthopaedic wards of the same hospital, Chan *et al.* (1979) observed an odds ratio [estimated by the Working Group] for use of kerosene stoves among all women of 1.6 (95% CI, 0.99–2.6) and among nonsmoking women of 2.1 (1.1–4.1).

Koo *et al.* (1983) conducted a case-control study of 200 hospitalized women with lung cancer and 200 control women from the general population matched for age, district of residence and type of housing. Odds ratios were estimated for different types and levels of exposure after controlling for smoking. Higher risks were observed among women with more than 30 years' use of kerosene for cooking (age-adjusted odds ratio for nonsmokers, 1.4; 95% CI, 1.1–1.9; $p=0.02$; odds ratio for smokers, 2.5; 1.2–5.4; $p=0.02$). Controls were more likely to have used liquid petroleum gas-type fuel.

[The Working Group considered that the predominant inhalation exposure of the women in these studies would have been to the combustion products of kerosene and not to the product itself. In view of a recent study from Shanghai, China (Gao *et al.*, 1987), exposure to cooking oil may have contributed to the observed effects.]

4. Summary of Data Reported and Evaluation¹

4.1 Exposure data

Fuel oils are complex and variable mixtures of alkanes and alkenes, cycloalkanes and aromatic hydrocarbons, containing low percentages of sulfur, nitrogen and oxygen compounds. Kerosene fuel oils are manufactured from straight-run petroleum distillates from the boiling range of kerosene [5]. Other distillate fuel oils contain straight-run middle distillate [6], often blended with straight-run gas oil [7] and light vacuum distillates [19], and light cracked distillates [24, 30]. The main components of residual fuel oils are the heavy residues from distillation and cracking operations [8, 21, 31]; various refinery by-products and heavy distillates [20, 26, 27] may be added. In fuel oils consisting mainly of atmospheric distillates, the content of three- to seven-ring polycyclic aromatic hydrocarbons is generally less than 5%. In fuel oils that contain high proportions of heavy atmospheric, vacuum and cracked distillates or atmospheric and vacuum residues, the content of three- to seven-ring polycyclic aromatic hydrocarbons may be as high as 10%; if large quantities of cracked components are incorporated, levels may approach 20%. Fuel oils are used mainly in industrial and domestic heating, as well as in the production of steam and electricity in power plants. Skin and inhalation exposures to fuel oil may occur during its production, storage, distribution and use and during maintenance of heating equipment. During the cleaning of fuel oil tanks, high, short-term exposures to total hydrocarbon vapours have been measured at levels ranging from 100–1600 mg/m³.

¹The numbers in square brackets are those assigned to the major process streams of petroleum refining in Table 2 of the monograph on occupational exposures in petroleum refining (p. 44).

4.2 Experimental data¹

A cracked bunker fuel was tested both alone and blended with the residue from the thermal cracking of catalytically cracked clarified oil [31] by skin application to mice. When applied alone, it induced benign and malignant skin tumours; a further increase was observed when cracked residue was added to the blend.

A West Texas uncracked residue [8 or 21] was tested alone or in combination with the residue described above [31]. When tested alone, it produced one skin papilloma, but a high incidence of skin papillomas and carcinomas was observed when cracked residue was added to the blend.

One sample of fuel oil No. 2 was tested by skin application to mice and produced skin carcinomas and papillomas.

Two samples of straight-run kerosene [5], one sample of light vacuum distillate [19], several samples of heavy vacuum distillates [20] and three samples of light catalytically cracked distillates [24] produced skin tumours in mice. Several heavy catalytically cracked distillates [26], residues of catalytically cracked clarified oils [27], thermally cracked residues [31] and steam-cracked residues [34] produced high incidences of benign and malignant skin tumours in mice. (See the monograph on occupational exposures in petroleum refining.)

4.3 Human data

Two large historical cohort studies of workers were conducted in Japan. In the first, an excess of lung cancer was observed among men exposed to kerosene, diesel oil, crude petroleum and mineral oil considered as a group. In the second, an excess of stomach cancer was observed among workers possibly exposed to kerosene, machine oil or grease. Leukaemia was reported to have occurred in excess in industries where kerosene, paraffin oil or petroleum combustibles were said to have been used or produced. Since none of the exposures could be defined clearly, these results are difficult to interpret.

In a large case-control study, a significant excess of colorectal cancer was associated with estimated exposure to solvents and fuel oil. In a second, an excess of stomach cancer was associated with exposure to kerosene, and excesses of rectal cancer and oat-cell lung cancer with exposure to heating oil.

Three case-control studies found a relationship between lung cancer and use of kerosene stoves for cooking in women in Hong Kong. No distinction was made between exposure to kerosene and exposure to its combustion products.

¹Subsequent to the meeting, the Secretariat became aware of one article accepted for publication in which it was reported that skin tumours developed in mice after skin application of furnace oil [probably fuel oil No. 2] in initiating/promoting studies (Gerhart *et al.*, 1988), and of another study in which it was reported that skin tumours developed in mice after skin application of several samples of commercial No. 2 heating oil [fuel oil No. 2] (Biles *et al.*, 1988).

4.4 Other relevant datas

Kerosene ingestion is a common cause of childhood poisoning and may result in lung damage.

No report specifically designed to study genetic and related effects in humans following exposure to fuel oil was available to the Working Group.

In single studies, kerosene did not induce chromosomal aberrations in rat bone marrow, nor did it induce mutation in cultured mammalian cells or in bacteria.

In single studies, fuel oil No. 2 induced chromosomal aberrations in rat bone marrow and mutation in cultured mammalian cells and in bacteria. Aromatic fractions of fuel oil No. 2 induced sister chromatid exchange, but not chromosomal aberrations, in cultured mammalian cells. One four- to seven-ring polycyclic aromatic hydrocarbon fraction of fuel oil No. 2 induced mutation in bacteria.

In single studies, a heavy fuel oil [B-class] induced chromosomal aberrations in cultured mammalian cells; bunker fuel did not induce mutation in bacteria or algae. (See Appendix 1.)

4.5 Evaluation¹

There is *inadequate evidence* for the carcinogenicity in humans of fuel oils.

There is *sufficient evidence* for the carcinogenicity in experimental animals of residual (heavy) fuel oils.

There is *limited evidence* for the carcinogenicity in experimental animals of fuel oil No. 2.

In formulating the overall evaluation, the Working Group also took note of the following supporting evidence reported in the monograph on occupational exposures in petroleum refining. There is *sufficient evidence* for the carcinogenicity in experimental animals of light and heavy catalytically cracked distillates, of light and heavy vacuum distillates and of cracked residues derived from the refining of crude oil. There is *limited evidence* for the carcinogenicity in experimental animals of straight-run kerosene.

Overall evaluation

Residual (heavy) fuel oils *are possibly carcinogenic to humans (Group 2B)*.

Distillate (light) fuel oils *are not classifiable as to their carcinogenicity to humans (Group 3)*.

¹For definitions of the italicized terms, see Preamble, pp. 24–28.

5. References

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