DIESEL FUELS

1. Chemical and Physical Data

1.1 Synonyms and trade names

Diesel fuel (general)

Chem. Abstr. Services Reg. No.: 68334-30-5
Chem. Abstr. Name: Diesel oil
IUPAC Systematic Name: –
Synonyms: Auto diesel; automotive diesel oil (ADO); derv; diesel; diesel fuel oil; diesel oil; gas oil

Diesel fuel No. 1

Chem. Abstr. Services Reg. No.: not assigned (essentially equivalent to kerosene, 8008-20-6)
Synonyms: Diesel fuel oil No. 1; diesel oil No. 1; No. 1 diesel (These designations are not used in European terminology. Where fuels similar to US diesel fuel No. 1 are available in Europe (Scandinavia), they are commonly referred to as kerosine or Arctic diesel. In some cases, non-descriptive terminology applies, e.g., dipolar in Sweden for special kerosene fuels used in urban areas.)

Diesel fuel No. 2

Chem. Abstr. Services Reg. No.: 68476-34-6 (applicable for specific viscosity limits)
Chem. Abstr. Name: No. 2 diesel fuel
Synonyms: Diesel fuel; diesel fuel oil No. 2; diesel oil No. 2; No. 2 diesel (term not used in Europe) In the UK, distillate fuels are frequently categorized as Class A1 (road diesel) and A2 (off-highway diesel).

Diesel fuel No. 4

Chem. Abstr. Services Reg. No.: not assigned
Synonyms: Marine diesel fuel; distillate marine diesel fuel

1.2 Description

The diesel engine and diesel fuel which provides the energy to run the engine derive their names from Rudolf Diesel, the German engineer who patented the engine design in 1892 (Anon., 1966). He operated his first successful engine in 1897 (Lane, 1980).

In its early history, the diesel engine was exploited for its versatility and ability to use a variety of cheap fuels. More recently, the requirements of efficiency and economics have prompted the development of fuel standards to meet desired performance characteristics, particularly for transportation service. Diesel fuels are appreciably less volatile than gasoline. They are classed as middle distillates and are more dense than gasoline, thus providing more energy per unit volume than gasoline. The product definition for diesel oil in the US Chemical Substances Inventory under the Toxic Substances Control Act is:

> *Diesel Oil* (CAS No. 68334-30-5) — A complex combination of hydrocarbons produced by the distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly in the range of C_9–C_{20} and boiling in the range of approximately 163–357°C.

In Europe, carbon numbers up to 28 and final boiling-points up to 390°C can be found for automotive diesel oil (CONCAWE, 1985).

The US definition encompasses both diesel fuel No. 1 and diesel fuel No. 2. There is no US Chemical Substances Inventory description for diesel fuel No. 1 or the equivalent European kerosene grade; however, in practice, this product is generally a straight-run petroleum distillate with a boiling range consistent with that of kerosene [5] (refer to Table 2 and Figure 1 of the monograph on occupational exposures in petroleum refining and to the monograph on jet fuel for the processing history of kerosene). Kerosene, and hence diesel fuel No. 1, consists of hydrocarbons with carbon numbers predominantly in the range of C_9–C_{16} and boiling in the range of approximately 150-300°C. Fuel oil No. 1 (heating) and kerosene used in Europe for heating applications have similar boiling ranges and are described in the monograph on fuel oils.

Diesel fuel No. 2 manufactured in the USA is generally a blend of straight-run and catalytically cracked streams, including straight-run kerosene [5], straight-run middle distillate [6], hydrodesulfurized middle distillate [6A] and light catalytically [24] and thermally cracked [30] distillates. The boiling range is generally approximately 160–360°C. The major component streams in European diesel fuels are presented in Table 1.

Diesel fuel No. 4 for low- and medium-speed engines, also characterized as a marine diesel fuel, is approximately similar to fuel oil No. 4 (CAS No. 68476-31-3), discussed in the monograph on fuel oils. As indicated in Table 2, American Society for Testing and Materials (ASTM) No. 4-D grade is more viscous than diesel fuel No. 2 and allows higher levels of ash and sulfur in the product. A No. 4 grade oil is generally classed as a residual fuel. It may be made either as a refinery stream which contains high boiling material classed as residual oil [8, 21, 31] or by blending residual fuel oil with a lighter material such as diesel fuel No. 2. In either case, it normally contains up to 15% residual oil components (CONCAWE, 1985). Some engines have been designed to operate on two different fuels,

Table 1. Major component streams of European automotive diesel oil (diesel fuel No. 2) and distillate marine diesel fuel (diesel fuel No. 4)[a]

TSCA Inventory name and identification number[b]	Refinery process stream (nomenclature used in Europe)	Automotive diesel oil (vol. %)	Distillate marine diesel fuel (vol. %)
	Straight-run (atmospheric) gas oil		
Straight-run middle distillate [6]	– light	40–100	40–100
Straight-run gas oil [7]	– heavy	0–3	0–50
Light vacuum distillate [19]	Vacuum gas oil	0–10	0–20
Light thermally cracked distillate [30]	Thermally cracked gas oil	0–20	0–30
Light catalytically cracked distillate [24]	Light catalytically cracked gas oil (cycle oil)	0–25	0–40

[a] From CONCAWE (1985)

[b] See Table 2 and Figure 1 in the monograph on occupational exposures in petroleum refining

with diesel fuel No. 2 used for idle and intermittent service and a No. 4 grade used for high-load, sustained operations (Guthrie, 1960).

Residual oil components are readily available at lower cost than distillate fuels and provide more energy per unit volume of product. These fuels are used in the same ways.

In general, the higher the content of straight-chain paraffins and paraffin side-chains in diesel fuels, the lower the autoignition temperature, and the higher the cetane number. However, waxy components tend to cause flow problems in very cold weather. Accordingly, more kerosene is often blended into winter grades of diesel fuel No. 2 to improve the flow properties. Diesel fuels are generally dried by passing through salt driers or water coalescers and filtered to remove rust and dirt.

1.3 Chemical composition and physical properties of technical products

Diesel fuel No. 1 is essentially equivalent to kerosene, the composition and properties of which are discussed in the monographs on jet fuel and fuel oils. It contains normal and branched-chain alkanes (paraffins), cycloalkanes (naphthenes), aromatics and mixed aromatic cycloalkanes. Normal alkanes usually predominate, resulting in a clean-burning diesel fuel with a relatively high cetane number. Cetane (*n*-hexadecane) gives excellent performance in diesel engines and was arbitrarily assigned the value of 100 in the cetane number scale (see Glossary); α-methylnaphthalene gives poor diesel engine performance and was assigned a value of zero (Lane, 1980).

The boiling range of diesel fuel No. 1 largely excludes the presence of benzene and polycyclic aromatic hydrocarbons. No direct data on concentrations were available to the

Table 2. Detailed requirements for diesel fuel oils (ASTM specification D 975[a]

Grade of diesel fuel oil		Flash-point °C (min)	Water and sediment vol. % (max)	Carbon residue on 10% residue % (max)	Ash weight % (max)	Distillation temperatures °C (90% point)		Viscosity				Sulfur weight % (max)	Copper strip corrosion	Cetane number (min)
								Kinematic cSt t 40°C (max)		Seybolt universal sec at 38°C[b]				
						min	max	min	max	min	max			
No. 1-D	A volatile distillate fuel oil for engines in service requiriing frequent speed and load changes	38	0.05	0.15	0.01	–	288	1.3	2.4	–	34.4	0.50	No. 3	40
No. 2-D	A distillate fuel oil of lower volatility for engines in industrial and heavy mobile service	52	0.05	0.35	0.01	282	338[b]	1.9	4.1	32.6	40.1	0.50	No. 3	40
No. 4-D	A fuel oil for low- and medium-speed engines	55	0.50	–	0.10	–	–	5.5	24.0	45.0	125.0	2.0	–	30

[a] Adapted from Lane (1980) and Hoffman (1982)

[b] Provided by American Petroleum Institute

Working Group, but kerosene which is approximately equivalent to diesel fuel No. 1 normally contains less than 0.02% benzene (CONCAWE, 1985; see IARC, 1982, 1987) and very low levels of three- to seven-ring polycyclic aromatic hydrocarbons (Dukek, 1978).

Because of the similarity of chemical composition, the discussion on fuel oil No. 2, in a separate monograph, is also generally applicable to diesel fuel No. 2 and European automotive diesel fuels. It contains normal and branched-chain alkanes (paraffins), cycloalkanes (naphthenes), aromatics and mixed aromatic cycloalkanes. Because it is likely to contain cracked stocks as one or more of the blend streams, it also contains olefins and mixed aromatic olefin types such as styrenes. Because of its more complex composition and lower percentage of straight-run fractions, diesel fuel No. 2 tends to have a lower cetane number than the No. 1 grade; however, cetane numbers can be improved by the use of additives.

Diesel fuel No. 2, when it consists predominantly of atmospheric distillate streams, contains possibly less than 5% of three- to seven-membered, condensed ring aromatic hydrocarbons (measured by the dimethyl sulfoxide extraction method of the Institute of Petroleum). In fuels that contain high proportions of heavy atmospheric, vacuum and light cracked distillates, the level may be as high as 10% (CONCAWE, 1985). Levels of some individual polycyclic aromatics in fuel oil No. 2 (which is approximately equivalent to diesel fuel No. 2) are given in Table 3 of the monograph on fuel oils. Some marine diesel fuels may contain more than 10% polycyclic aromatic hydrocarbons (CONCAWE, 1985; see also the monograph on fuel oils). Diesel fuels may also contain minor amount of constituents such as *n*-hexane (below 0.1%), benzene (below 0.02%), toluene, xylenes and ethyl benzene (0.25–0.5%).

Refiners normally select blend stocks to ensure easy starting and smooth engine performance. Sulfur, nitrogen and oxygen compounds are present as impurities in these streams, but their presence can be limited by hydrotreating and other processes. Because No. 2 diesel fuel, and European automotive diesel fuels in particular, normally contains minor quantities of olefins, the stability of the product in storage is of concern. Fuel degradation products formed during long-term storage can result in troublesome contamination. High temperatures and oil-soluble metal compounds (particularly those containing copper) can hasten degradation. Storage in the presence of water promotes bacterial growth which can result in sludge. Refiners generally prefer not to use additives in diesel fuel, although they can improve and preserve its quality.

Cetane improvers, such as organic nitrates, can be added to improve the ignition quality of the product. Oxidation inhibitors are added to prevent product degradation; corrosion inhibitors and metal deactivators can be added as required. Biocides are sometimes used when bacterial growth in storage may be a problem, and rust inhibitors can be added to minimize corrosion, particularly in storage facilities. Additives such as cetane improvers and oxidation inhibitors are usually added to normal production volumes by refiners; the use and concentration of other additives may be agreed by the supplier and the purchaser. A wide range of additives may be employed to assure satisfactory technical performance; examples are shown in Table 3. Military specifications for diesel fuels include many additives (US Navy, 1985).

Table 3. Examples of additives used in diesel fuels[a]

Flow improvers: ethylene/vinyl acetate polymers — about 500 ppm max
– long-chain polyester derived from acetic acid and unsaturated C_{16} alcohol
– polyolefin ester derived from 2-ethylhexyl acrylate

Antistatics: used typically at 1–5 ppm
– Cr and Ca salts of mono- and di-alkyl salicylic and dodecyl sulfosuccinic acids
– toluene, alkyl benzene sulfonate, high mol. wt polysulfone, polyamine
– polyamide, carboxylate, carboxylic acid in aromatic oil

Other additives:

Antioxidant	2,4-Dimethyl-6-*tert*-butylphenol	9–25 ppm
Stability improver	Polymethacrylate, polyisobutene, alkanolamine, amide, carboxylate	50 ppm
Ash modifier	Zinc diaryl dithiophosphate, phenols, carboxylate	300 ppm
Ignition (cetane) improver	Organic nitrates (e.g., isopropyl nitrate)	200–800 ppm
Multi-purpose	Styrene/ester copolymer	20–200 ppm
Antiwear	Polymeric ester	0.1 vol%
Lubricity improver	Phosphate ester amide, neutralized with long chain amine	0.03 wt%
Metal deactivator	*N*,*N*′-Disalicylidene-1,2-propanediamine	5.8 mg/l
Biocides	Thiazine derivatives	

[a]Provided by CONCAWE

Performance requirements for diesel fuels are defined primarily in terms of physical tests rather than chemical composition. Table 2 lists the ASTM D 975 test specifications for diesel fuels; Tables 4 and 5 (compiled by CONCAWE) give a summary of the European national standards by country, including kerosene standards (similar to ASTM No. 1).

The discussions here and in the monograph on fuel oils regarding composition and processing of fuel oils are generally applicable to gas turbine fuel oils, except in those instances where the inclusion of residual components is permitted.

Table 4. Compilation of national industrial standards and regulatory requirements for kerosene (1986)

Country	National Standards Reference (date)	Flash-point		Smoke point mm (min)	Wick char °C (min)	Density at 15°C kg/m^3 (max)	Kinematic viscosity at 40°C mm^2/sec	Sulfur mass % (max)	Distillation
		IP 170[a] °C (min)	D56[b] °C (max)						
Germany, Federal Republic of	DIN 51 636A		40			830		0.07	initial boiling-point, 130°C min 10% max at 150°C 95% min at 280°C
Italy	UNI 6579 (1977)		21			770–820		0.25	90% max at 210°C 65% min at 250°C
United Kingdom	BS 2869 C2 (1983)	38		20	20		1.0–2.0	0.20	15% min at 200°C final boiling-point, 300°C max

[a] UK Institute of Petroleum Method IP 170

[b] ASTM method D56

Table 5. National industrial standards and regulatory requirements for automotive diesel fuel (1986)

	Austria	Belgium & Luxembourg	France	Germany, F.R.	Ireland	Italy	Netherlands[a]	Norway	Switzerland	United Kindgdom	
National Standard reference (date)	ONORM C1104[b] (1986)	NBN 52-501[c] (1969)	CSR 0.9-1 (1986)	DIN 51.601 (1986)	IS 251 (1981)	NC 630 01[b] (1985)	No national standard	No national standard	SNV 181160/1 (1985)	BS 2869 A1[d]	A2[e]
Cetane no. index (min)	45	–	50[f]	45	–	47	–	–	48[g]	50	45
Cetane index (min)	–	–	–	–	–	48	–	–	48[g]	–	–
Cloud-point W (S)[h] °C (max)	–	–	0 (–)	–	0 (–)	–	–	–	−6 (−6)[g]	–	–
Pour-point W (S) °C (max)	–	−6 (–)	−12 (−7)	–	–	−6 (−6)	–	–	−15 (−9)	–	–
Cold filter plugging point W (S) °C (max)	−15 (+5)	–	−12 (0)[i]	−15(0)	−9 (–)[j]	−10 (–)	–	–	−15 (−8)[g]	−9 (0)	−12 (−4)
Density at 15°C (kg/m^3)	Report	–	810–890	820–860	810–860	805–865	–	–	815–860	–	–
Flash-point PM[k] °C (min)	55	50	55–120	55	55	55	55	60[l]	55	56	56
Kinematic viscosity at 20°C (mm^2/sec)	3.0–8.0	7.4 max	9.5 max	2.0–8.0	–	2.0–5.35	–	–	3.0–6.0	–	–
at 40°C (mm^2/sec)	–	–	–	–	1.5–6.0	–	–	–	–	1.5–5.0	1.5–5.5
Sulfur mass % (max)	0.15	0.3	0.3	0.3[m]	0.5	0.3[b]	0.3	0.5[n]	0.3[o]	0.3	0.5[p]
Distillation	90% min at 350°C	65% max at 250°C 85% min at 350°C	65% max at 250°C 85% min at 350°C	65% max at 250°C 85% min at 250°C	Initial boiling-point, 170°C min Final boiling-point, 380°C max	2% max at 150°C 65% max at 250°C 85% min at 350°C	65% min at 250°C 85% min at 350°C	–	90% max at 360°C	85% min at 350°C	85% min at 350°C
Water (max)	–	–	Trace	0.05 mass %	0.04 mass %	–	–	–	–	0.05 vol %	0.05 vol %
Sediment (max)	–	–	Nil	–	–	–	–	–	–	0.01 mass %	0.01 mass %
Water and sediment (max)	–	0.10	–	–	–	0.05 vol %	–	–	Nil	–	–
Ash mass % (max)	0.01	–	Trace	0.02	–	0.01	–	–	0.005	0.01	0.01

Table 5 (contd)

	Austria	Belgium & Luxembourg	France	Germany, F.R.	Ireland	Italy	Netherlands[a]	Norway	Switzerland	United Kindgdom	
Carbon residue[q]										A1	A2
Mass % (max) 10% bottoms mass % (max)	0.25 (C)	–	–	–	–	0.15 (C)	–	–	0.05 (C)	0.2 (R)	0.2 (R)
Strong acid no.	–	–	Nil	–	–	–	–	–	–	–	–
Copper strip corrosion rating	1b max (3 h at 100°C)	–	–	–	–	2 max (3 h at 50°C)	–	–	–	1 max (3 h at 100°C)	1 max (3 h at 100°C)
Neutralization no. mg KOH/g (max)	0.15	–	–	–	–	–	–	–	–	–	–
Dyes and markers	None	None	None	None	None	None	None	None	None	None	Red dye and quinzarin

[a] Industrial and EEC customs standards

[b] Revised standard

[c] New standard under discussion

[d] A1 for automotive use (BS2869, 1983); revision under review

[e] A2 for stationary units (BS2869, revised 1986); revised standard

[f] 50 min summer, 48 min winter; revision to 48 min all year under review, with further relaxation to 45 under study

[g] Alternative standard

[h] W, winter; S, summer

[i] –18°C capability with additional flow improver

[j] Alternative is –7°C max cloud-point

[k] Pensky-Martens method

[l] Government regulation

[m] Reduction to 0.1–0.15 mass % likely around 1988

[n] By agreement

[o] 0.2 mass % max from July 1987

[p] 0.3 mass % expected around 1988

[q] C, Conradson; R, Ramsbottom method of measurement

2. Production, Use, Occurrence and Analysis

2.1 Production and use

(a) Production and consumption

As the product name suggests, diesel fuels are designed for use as fuels in diesel engines. The No. 1 grade is the more volatile of the two principal grades and gives good performance in engines requiring frequent changes in speed and load, such as city buses. It is also the cleaner burning of the two grades. The No. 2 grade has a higher specific gravity, providing more energy per unit volume of fuel, which is an important economic factor in industrial and heavy transportation service such as railroads, trucks and river boats. Hence the major growth in consumption has been in the No. 2 grade. Diesel fuel No. 4 is a special grade of fuel oil for low- and medium-speed engines that can use a more viscous fuel oil with a relatively high sulfur content (max, 2.0 wt %; Lane, 1980).

The conversion of railroads to diesel engines accelerated in the 1940s and continued after the Second World War, after which time there was a rapid conversion of trucks to diesel service. Today, most heavy duty transportation is powered by diesel engines. Although the conversion of automobiles to diesel service has been very limited in the USA, cars powered by diesel engines are used extensively in Europe, where diesel car registrations accounted for 3.8% of new passenger cars in 1977, 6.9% in 1980 and 17.5% in 1986 (data provided by CONCAWE).

Production and consumption of diesel fuels combined as one class of product for the USA and for the 24 countries included in the Organisation for Economic Cooperation and Development (OECD) combined are presented in Table 6, and cover the period 1970–1985 in five-year increments (International Energy Agency, 1987). Continued growth in demand for diesel fuel is reflected by the data until 1980.

Table 6. Production and consumption (in thousands of tonnes) of diesel fuel[a] in the USA and in countries of the Organisation for Economic Cooperation and Development (OECD) for 1970–85[b]

Area	Production/ consumption	1970	1975	1980	1985
USA	Production	120 254	134 967	138 323	135 181
	Consumption	120 151	133 300	136 161	130 297
OECD	Production	336 688	370 240	408 848	372 728
	Consumption	336 678	380 181	403 642	386 081

[a] Including gas oils in Europe

[b] From International Energy Agency (1987)

Data on production and consumption of diesel fuels for 1985 are listed by geographical area in Table 7.

Table 7. Production and consumption (in thousands of tonnes of diesel fuel[a] by geographical area, 1985[b]

Region or organization	Production	Consumption
North America	154 368	149 427
USA	135 181	130 297
Canada	19 187	19 130
OECD (Europe)	173 474	190 960
European Economic Community	152 091	163 132
Pacific[c]	44 886	45 694
OECD (All)	372 728	386 081

[a] Including gas oils in Europe

[b] From International Energy Agency (1987)

[c] Australia, Japan, New Zealand

(b) Use

Diesel Fuel No. 4 is used in railroads, to move river barges and for stationary engines in continuous, high-load service. In addition to their principal use as transportation fuels, diesel fuels are used in stationary gas turbines, for example, to generate electic power during peak load periods. Distillate fuel oils defined by ASTM Specification D 396 (see monograph on fuel oils) are also used in stationary gas turbines. While the respective basic grades of fuel oils and diesel fuel are similar, there are specific requirements that are important for gas turbine service.

(c) Regulatory status and guidelines

No data were available on occupational exposure limits for diesel fuel.

2.2 Occurrence

(a) Occupational exposure

Occupational exposure to diesel fuel (diesel oil) has been associated with the following operations (CONCAWE, 1985): manually handled filling and discharge; marine diesel bunkering involving the manual handling of discharge lines; retailing through filling stations; tank dipping, pipeline and pump repairs, filter cleaning in refineries, distribution terminals and depots; tank inspection, cleaning and repairing; manufacture, repair, servicing and testing of diesel engines or equipment and injection and fuel systems; routine sampling and laboratory handling of diesel oils; and practices in which diesel oils are used as cleaning agents or solvents.

Because of their low volatility, at normal temperatures diesel fuels should generate vapours at only low concentrations, except in confined spaces. High operating temperatures could result in significant vapour concentrations and, as in the case of residual fuel oils, in the evolution of hydrogen sulfide gas (CONCAWE, 1985). No published quantitative data on exposure levels to diesel fuel were available to the Working Group.

(*b*) *Environmental exposure*

Table 8 lists some accidental releases of diesel fuel that have been reported in the recent past.

Table 8. Examples of major accidental releases of diesel fuel

Place	Date	Type	Quantity	Reference
Spitzbergen, Norway	April–May 1978	Rupture of diesel fuel storage tank	130 m^3	Carstens & Sendstad (1979)
Queen Charlotte Islands, Canada	March 1984	Barge spill	130 tonnes	McLaren (1985)
Yaquina Bay, OR, USA	November 1983	Diesel fuel and bunker C fuel oil from wreck of tanker, *Blue Magpie*	284 000 l	Kemp *et al.* (1986)
Floreffe, PA, USA	December 1987	Rupture of diesel fuel storage tank	3 million gallons (11.4 million l)	MacKerron & Kiesche (1988)

2.3 Analysis

Since diesel fuel is composed of a complex mixture of hydrocarbons, there are few methods for the environmental analysis of 'diesel fuel' as an entity, but many methods are reported for the analysis of its component hydrocarbons. These methods are used to identify or 'fingerprint' the origin of a specific diesel fuel sample on the basis of the proportions of its component hydrocarbons. No specific method for the sampling and analysis of diesel fuel vapours was available.

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], which is a component of diesel fuel Nos 1 and 2, and of light catalytically cracked distillates [24] and light vacuum distillate [19], which are used in diesel oil Nos 2 and 4, are described in the monograph on occupational exposures in petroleum refining. Studies on residues of thermally cracked oils [31], which may be used in diesel fuel No. 4, are also described in that monograph.

Skin application

Mouse: Groups of 49 or 50 male and 50 female B6C3F1 mice, eight weeks old, were administered 250 or 500 mg/kg bw marine diesel fuel in 0.1 ml acetone by application to clipped interscapular dorsal skin on five days per week for 103 weeks or 84 weeks (high-dose group terminated due to severe ulceration of the skin), respectively. A control group received the vehicle only. The diesel fuel was a mixture of petroleum-derived hydrocarbons containing 12.7% paraffins and 87.3% aromatic compounds. Survival at 84 weeks was 26/50 and 29/50 among high-dose males and females, respectively; at 104 weeks, survival was 20/49 and 12/50 in low-dose males and females, and 30/50 and 40/50 among vehicle-control males and females, respectively. There was a significant increase in the incidence of squamous-cell papillomas and carcinomas at the application site in males (controls, 0/49; low-dose, 0/49; high-dose, 3/49 (two carcinomas; $p = 0.019$). The incidences of these tumours at the adjacent inguinal site in males were: controls, 1/50 (papilloma); low-dose, 2/49 (carcinomas); high-dose, 0/50. The incidences of squamous-cell carcinomas at the application site in females were: controls, 0/50; low-dose, 1/45; high-dose, 2/48; no papilloma occurred, and no tumour was found at the adjacent inguinal region. Although no data on historical controls were available for acetone-treated animals of this strain, the background rate for skin neoplasms among untreated mice is quite low (<1%). The incidences of hepatocellular adenomas in males were: control, 5/50; low-dose, 10/48; high-dose, 10/49. The total numbers of male mice with hepatocellular tumours (adenomas and carcinomas combined) were: controls, 9/50; low-dose, 17/48; high-dose, 14/49 ($p = 0.035$). The incidence of hepatocellular tumours did not differ significantly from that in historical controls (540/1784; 30 ± 8%; National Toxicology Program, 1986).

3.2 Other relevant data

(*a*) *Experimental systems*

Absorption, distribution, excretion and metabolism

No data on the absorption, distribution, excretion and metabolism of diesel fuel in laboratory animals were available to the Working Group. One study has been reported on gulls and ducks (McEwan & Whitehead, 1980).

Toxic effects

The oral LD_{50} of diesel fuel [unspecified] in rats was 7.5 g/kg bw. No mortality was induced in acute dermal toxicity studies in rats dosed at 5 g/kg bw (Beck *et al.*, 1984).

Groups of male and female B6C3F1 mice were administered 2000–40 000 mg/kg bw 100% marine diesel fuel by dermal application for 14 consecutive days. No animal treated with 20 000 or 40 000 mg/kg survived. Skin lesions were similar in all dosed groups —

moderate acanthosis, parakeratosis and hyperkeratosis, accompanied by mixed cellular inflammatory infiltrate in the upper dermis (National Toxicology Program, 1986).

Groups of male and female B6C3F1 mice were administered 250–2000 mg/kg bw marine diesel fuel in acetone or 4000 mg/kg 100% marine diesel fuel by dermal application on five days per week for 13 weeks; no treatment-related death occurred. An increased severity of mild chronic active dermatitis at the site of application was observed in the high-dose group (National Toxicology Program, 1986).

Groups of male and female B6C3F1 mice were administered 250 or 500 mg/kg bw marine diesel fuel in acetone by dermal application on five days per week for 103 weeks (84 weeks for high-dose groups; early termination was due to ulceration of the skin). Increases in haematopoiesis were found in the spleen in animals of each sex and in the liver in females. Increases in plasmacytosis occurred in lymph nodes in females and in high-dose males. Ulcers and chronic dermatitis were observed at increased rates at the site of dermal application and in the inguinal region of the skin (National Toxicology Program, 1986).

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 400 ppm diesel fuel [unspecified] resulted in no teratogenic effect (Schreiner, 1984). [The Working Group noted that details were not reported.]

Genetic and related effects

Diesel fuel (boiling range, 186–357°C; 24% aromatics) was found to be weakly mutagenic to *Salmonella typhimurium* TA98 using the suspension method (3.38–25 μl/ml) but not using the plate incorporation method (0.001–5 μl/plate), in the presence and absence of an exogenous metabolic system from rat liver (Conaway *et al.*, 1984). Diesel 25 [not further specified] was not mutagenic to *S. typhimurium* TA1535, TA1538, TA98 or TA100 (plate test; Vandermeulen *et al.*, 1985), or to *Chlamydomonas reinhardtii* in a forward mutation assay (streptomycin resistance; Vandermeulen & Lee, 1986). Marine diesel fuel was not mutagenic to *S. typhimurium* TA1935, TA1937, TA98 or TA100 in the presence or absence of Aroclor 1254-induced rat or hamster liver microsomes (National Toxicology Program, 1986).

Neither aliphatic nor aromatic fractions separated from diesel fuel No. 7911 [not further specified] by dimethyl sulfoxide induced mutation in *S. typhimurium* TA100 (Henderson *et al.*, 1981).

Diesel fuel (boiling range, 186–375°C; 24% aromatics) was not mutagenic to L5178Y $TK^{+/-}$ mouse lymphoma cells either in the presence or absence of an exogenous metabolic system from either rat or mouse liver. Undiluted diesel fuel increased the frequency of chromosomal aberrations in the bone marrow of Sprague-Dawley rats 6–48 h after a single intraperitoneal injection of 2 or 6 ml/kg bw or after five daily intraperitoneal injections of 2 or 6 ml/kg bw per day (Conaway *et al.*, 1984).

(*b*) *Humans*

Absorption, distribution, excretion and metabolism

Absorption was assumed to have occurred mainly through the skin of a 28-year-old sailor who developed symptoms of intoxication after using diesel fuel as a shampoo (Barrientos *et al.*, 1977).

Toxic effects

Anuria, renal failure and gastrointestinal symptoms developed several hours after the incident described above; the sailor recovered after dialysis. A renal biopsy on the second day showed tubular dilatation with casts, flattening of epithelial cells, mitosis and vacuolization (Barrientos *et al.*, 1977).

A man who cleaned his hands and arms with diesel fuel over several weeks developed renal failure over about three months. Renal biopsy showed acute tubular damage, with patchy degeneration and necrosis of proximal and distal tubular epithelium and preservation of basement membranes (Crisp *et al.*, 1979).

Cutaneous hyperkeratosis has been described in engine drivers exposed occupationally to diesel fuel (Gusein-Zade, 1974).

A young woman who claimed to have ingested a large amount of diesel fuel (1.5 l) in a suicidal attempt developed toxic lung disease over the next few days, with fever, dry cough and basal opacities on chest X-ray. The condition resolved over the following four months (Boudet *et al.*, 1983).

A woman aged 28 years who accidentally inhaled diesel fuel immediately began to cough, became dyspnoeic and cyanosed and lost consciousness for 1 h. A productive cough with sputum smelling of diesel fuel persisted for 37 days. Chest X-ray showed diffuse shadowing, most prominent at the lung bases, which resolved slowly with treatment but was still present at day 37. Blood biochemistry indicated slight hepatotoxic effects but with no clinical problem (Perez Rodriguez *et al.*, 1976).

Effects on reproduction and prenatal toxicity

No data were available to the Working Group.

Genetic and related effects

A group of 12 diesel vehicle drivers (six smokers and six nonsmokers) exposed to vehicle exhausts and to fuel, among other agents, was studied for cytogenetic changes. The nonsmoking drivers were reported to have more chromosomal aberrations (mean, 3.6% aberrant cells) than nonsmoking gasoline-vehicle drivers and nonsmoking unexposed controls (mean, 1.4% aberrant cells). [The Working Group noted that a 72-h culture time was used in this study.] No difference between the groups was noted in the frequency of sister chromatid exchange, although smokers in all groups had significantly higher mean frequencies than nonsmokers (Fredga *et al.*, 1982). [The Working Group noted the small size of the group and the mixed exposure of the workers.]

3.3 Epidemiological studies and case reports of carcinogenicity to humans

The studies reviewed in the monograph on gasoline often involved subjects or occupational groups with mixed exposures, particularly to gasoline and diesel fuel. It was often not possible to separate the effects of the two types of fuel. Studies that primarily addressed the risk associated with exposure to combustion products of diesel fuel are not considered here but are the subject of *IARC Monographs* Vol. 46 (IARC, 1989).

In a case-control study of cancer at many sites in Montréal, Canada, described in detail in the monograph on gasoline (p. 185), an increased risk for cancer of the prostate, with an adjusted odds ratio of 1.9 (90% confidence interval (CI), 1.2–3.0), was observed among men exposed to diesel fuel; however, there was no evidence of a positive dose-response relationship (Siemiatycki *et al.*, 1987). There was an increased risk for squamous-cell carcinoma of the lung in men exposed to diesel fuel (adjusted odds ratio (including smoking), 1.6; 90% CI, 1.0–2.6); for men with estimated 'nonsubstantial' exposure, the odds ratio was 1.0 (0.4–2.0), and for those with 'substantial' exposure, it was 2.5 (1.3–4.7). Mechanics and repairmen, who constituted the largest group exposed to diesel fuel, had an adjusted odds ratio of 2.0 (0.9–4.2). [The Working Group noted that, in the interpretation of the lung cancer risks, no attempt was made to separate the effects of exposure to combustion products from those of exposure to the liquid itself.]

4. Summary of Data Reported and Evaluation[1]

4.1 Exposure data

Diesel fuels are complex mixtures of alkanes, cycloalkanes and aromatic hydrocarbons with carbon numbers in the range of C_9–C_{28} and with a boiling-range of 150–390°C. Kerosene-type diesel fuel (diesel fuel No. 1) is manufactured from straight-run petroleum distillates [5]. Automotive and railroad diesel fuel (diesel fuel No. 2) contains straight-run middle distillate [6], often blended with straight-run kerosene [5], straight-run gas oil [7], light vacuum distillate [19] and light thermally cracked [30] or light catalytically cracked distillates [24]. Some blended marine diesel fuels also contain heavy residues from distillation [8, 21] and thermal cracking [31] operations. In diesel fuel consisting mainly of atmospheric distillates, the content of three- to seven-ring polycyclic aromatic hydrocarbons is generally less than 5%; in diesel fuel that contains high proportions of heavy atmospheric, vacuum and light cracked distillates, the content of such polycyclic aromatic hydrocarbons may be as high as 10%. Some marine diesel fuels may contain higher levels. Saleable diesel fuel may also contain a variety of additives, such as organic nitrates, amines, phenols and polymeric substances. Exposure to diesel fuel through the skin and by inhalation may occur during its production, storage, distribution and use as well as during maintenance of diesel engines.

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[1] The 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 data[1]

One sample of marine diesel fuel was tested for carcinogenicity in one strain of mice by skin application, producing a few squamous-cell carcinomas and papillomas at the application site in animals of each sex and a few carcinomas at the adjacent inguinal region in males.

Two samples of straight-run kerosene [5], one sample of light vacuum distillate [19] and three samples of light catalytically cracked distillate [24] produced skin tumours in mice. Some residues from thermal cracking [31] produced benign and malignant skin tumours in mice. (See the monograph on occupational exposures in petroleum refining.)

4.3 Human data

In a case-control study of cancer at many sites, there was evidence of an increased risk for squamous-cell carcinoma of the lung in men estimated to have had substantial exposure to diesel fuel. There was also an indication of an increased risk for cancer of the prostate. No attempt was made to separate the effects of combustion products from those of exposure to diesel fuel itself.

4.4 Other relevant data

Inhalation or ingestion of diesel fuel resulted in acute and persistent lung damage in humans.

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

Application of marine diesel fuel to the skin of mice resulted in ulceration.

In a single study, diesel fuel induced chromosomal aberrations in bone-marrow cells of rats; it did not induce mutation in cultured mammalian cells but was weakly mutagenic to bacteria. Another sample did not induce mutation in bacteria or algae; a sample of marine diesel fuel and aliphatic and aromatic fractions of an unspecified diesel fuel were also not mutagenic to bacteria. (See Appendix 1.)

4.5 Evaluation[2]

There is *inadequate evidence* for the carcinogenicity in humans of diesel fuels.

There is *limited evidence* for the carcinogenicity in experimental animals of marine diesel fuel.

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[1] Subsequent to the meeting, the secretariat became aware of a study in which skin tumours were reported in mice after application to the skin of petroleum diesel (boiling range, 198–343°C) [corresponding to diesel fuel No. 2] (Clark *et al.*, 1988).

[2] For definitions of the italicized terms, see Preamble, pp. 24–28.

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 *limited evidence* for the carcinogenicity in experimental animals of straight-run kerosene and *sufficient evidence* for the carcinogenicity in experimental animals of light vacuum distillates, of light catalytically cracked distillates and of cracked residues derived from the refining of crude oil.

Overall evaluation

Marine diesel fuel *is possibly carcinogenic to humans (Group 2B).*

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

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