SOME PETROLEUM SOLVENTS[1]

1. Chemical and Physical Data[2]

1.1 Synonyms

The petroleum solvents covered in this monograph are all complex mixtures of hydrocarbons produced from petroleum distillation fractions which have been further refined by one or more process. Unlike petroleum fuels (IARC, 1989), these mixtures are not produced by blending various refinery process streams but rather by further refining and distilling one or two streams to make a product significantly different in chemical composition and much narrower in boiling range (typically 15–30°C) than its source streams.

Petroleum solvents are generally defined and differentiated by certain physical properties and by chemical composition. Among the properties of importance, depending on the intended end–use of the solvent, are boiling range, flash–point, solvent strength (solvency), colour, odour, aromatic content and sulfur content. Some of these properties are interrelated; for example, increasing the aromatic content often increases solvency, but also increases odour. In addition, the same property may be measured in different ways in different industries or in different geographic regions; for example, kauri–butanol value (the amount of petroleum solvent in millilitres required to cause cloudiness in a solution of kauri gum and *n*–butanol) and aniline point (the minimal temperature for complete mixing of aniline with a petroleum solvent) are both indicators of solvency but kauri–butanol value is more commonly used in Europe and aniline point more commonly in the USA.

It is not surprising, then, that the same names may be used for solvents that are not identical, and that different classification systems or names may be more common in one industry or geographic region than another. 'White spirits', for example, is a common term in Europe but is seldom used in the USA. The following paragraphs provide a brief overview of

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[1] Saleable, petroleum–derived hydrocarbon mixtures used principally as solvents

[2] Much of the material presented in this section and in sections 2.1 and 2.3 is taken from reports prepared by CONCAWE (the oil companies' European organization for environmental and health protection), in collaboration with the European Chemical Industry Ecology and Toxicology Centre, and the American Petroleum Institute; in these cases, no reference is given.

the classification system adopted for this monograph. The vagaries in the names used for petroleum solvents, however, make it important that some physical/chemical properties be included in any discussion of their toxic effects.

The petroleum solvents covered in this monograph are grouped in three classes generally based on volatility and aromatic content (which is related to solvency). These classes (special boiling range solvents, white spirits and high-boiling aromatic solvents) are widely adopted industrial categories. Figure 1 shows the general relationship among these three broad categories of petroleum solvents, with respect to carbon number, boiling range and solvency.

Common names for various products

Special boiling-range solvents: Benzine; canadol; essence; high-boiling petroleum ether; lacquer diluent; light ligroin; ligroin; naphtha; naphtha 76; petroleum benzin; petroleum ether; refined solvent naphtha; rubber solvent; SBP; special boiling-point solvents; special naphtholite; spezialbenzine; varnish makers' and painters' naphtha; VM & P naphtha [CAS No. 8030-30-6 (National Institute for Occupational Safety and Health); 8032-32-4 (American Conference of Govermental Industrial Hygienists)]

White spirits: DAWS; dearomatized white spirits; 140 flash solvent; HAWS; high aromatic white spirits; kristalloel; lacquer petrol; LAWS; light petrol; low aromatic white spirits; mineral solvent; mineral spirits; mineral turpentine; odourless mineral spirit; petroleum spirits; solvent naphtha; Stoddard solvent [CAS No. 8052-41-3]; terpentina; turpentine substitute

High-boiling aromatic solvents: Naphtha

1.2 Chemical and physical properties

Calculation of conversion factors for converting air concentrations expressed in parts per million to milligrams per cubic metre requires knowledge of the molecular weight of a chemical. Since the molecular weights of complex and variable mixtures such as petroleum solvents cannot be specified, conversion factors have not been included in this monograph. It is noted, however, that, for practical purposes, others have used average molecular weights to generate approximate conversion factors for certain well-defined petroleum solvents (American Conference of Governmental Industrial Hygienists, 1988).

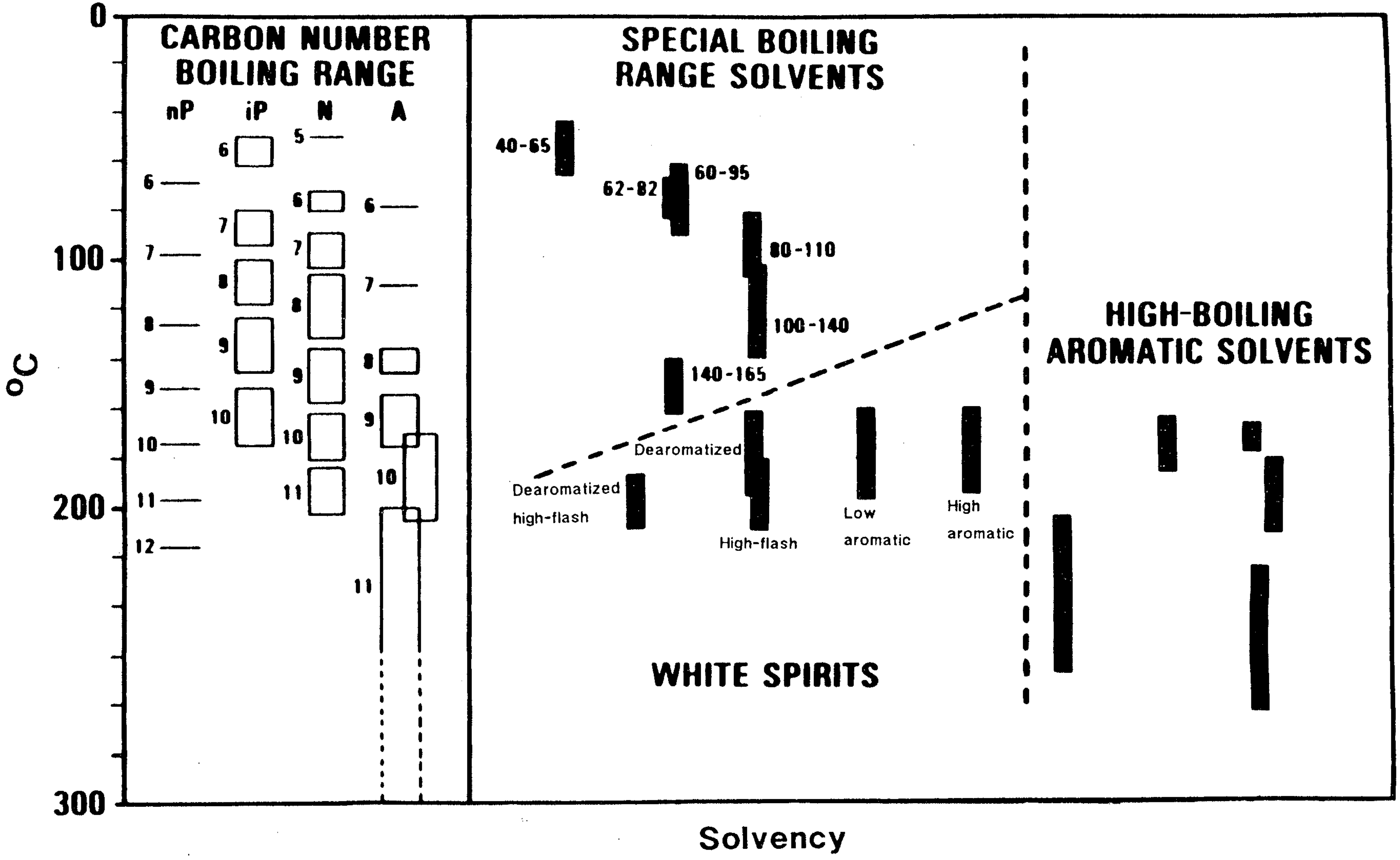
Undated references in parentheses used in sections 1.2 and 1.3 are to national and international specifications as follows: ASTM, American Society for Testing and Materials; BS, British Standards; DIN, Deutsche Industrie-Norm (German Industrial Standard); ISO; International Standards Organization; NF, National Formulary (USA).

(*a*) *Special boiling-range solvents*

Three main types of special boiling-range solvents may be distinguished with regard to production processes:

Type 1 – hydrodesulfurized special boiling-range solvents, which can contain up to 20 wt% aromatic compounds;

Fig. 1. Relationships among the three categories of petroleum solvents[a]



[a] nP, normal paraffins; iP; isoparaffins; N, naphthenic compounds; A, alkyl benzenes

Type 2 – hydrogenated special boiling-range solvents, in which the aromatic compounds have been converted to alicyclic hydrocarbons and the aromatic content is less than 0.02 wt%; and

Type 3 – hydrogenated special boiling-range solvents, to which aromatic compounds (often toluene) are added and which may have an aromatic content of up to 50 wt%.

(i) *Description*: Clear, colourless hydrocarbon solvent

(ii) *Boiling range*: 30–160°C (ASTM D1078, ASTM D850, ASTM D86-82, DIN 51751, NF MO7-002)

(iii) *Density*: 0.670–0.760 at 15°C (ASTM D1298, ASTM D3505, ASTM D4052-81, ASTM D891, ASTM D1250, DIN 51757, NF T60-101)

(iv) *Refractive index*: 1.37–1.42 at 20°C (ASTM D1218-82, DIN 53169)

(v) *Solubility*: Less than 0.1 wt% in water

(vi) *Viscosity*: 0.3–0.75 cps at 25°C (ASTM D445-83, DIN 51562, DIN 53015)

(vii) *Volatility*: 19–0.6; relative evaporation rate, *n*-butyl acetate = 1 (ASTM D3539, DIN 53170)

(viii) *Reactivity*: Reacts with strong oxidizing agents

(ix) *Kauri-butanol value*: 30–36 (ASTM D1133)

(x) *Aniline point*: 60–64°C (ASTM D611-82, DIN 51775, NF MO7-021)

(xi) *Flash-point*: <0–32°C (ASTM D56, ASTM D93-80, DIN 51755)

(xii) *Colour (with a Saybolt colorimeter)*: +30 (ASTM D156-82, DIN 51411)

(xiii) *Carbon number range*: 4–11

(*b*) *White spirits*

The nomenclature of hydrocarbon solvents produced as distillates in the normal refining of petroleum and used, for example, in the coatings, paints and dry-cleaning industries, is vague and confusing. Commercial names may not therefore indicate composition. In Europe, the name encountered most often is 'white spirits', an alternative synonym being 'mineral solvent'. In the USA, the name used most commonly for these solvents is 'mineral spirits'. 'Mineral spirits: type 1 – regular', as specified by ASTM D235, is 'Stoddard solvent' which is similar in composition to the product generally recognized in Europe as white spirits. The terms 'solvent naphtha' and 'turpentine substitute' are used to describe the same materials.

The solvent generally recognized in Europe as white spirits, and that to which the general public is most likely to be exposed in its applications as a paint thinner and brush cleaner, is a petroleum distillate that boils typically in the range 150–205°C with a typical aromatic content of 15–25%. However, products of this composition in the UK are deemed to be 'low aromatics', whereas in France a 'low aromatic white spirit' is one with an aromatic content of 5% or less. In the USA, the latter would be 'type 3 - odourless mineral spirits' (ASTM D235), which has a maximal kauri-butanol value of 29 rather than a limit on aromatic content. Some white spirits of even lower aromatic content (typically less than 1%) are produced by treatment with hydrogen (hydrogenation) in the presence of a catalyst. 'High aromatic white spirit', with a typical aromatic content of 45%, is both specified (ISO 1250, BS 245) and commercially available in Europe.

Three main types of white spirits may be distinguished with regard to production processes:

Type 1 – hydrodesulfurized white spirits, which generally contain 15–25 wt% of aromatic compounds but may contain up to 45 wt%; in the USA, the aromatic content of such solvents rarely exceeds 15–16% and is often much lower;

Type 2 – solvent-extracted hydrodesulfurized white spirits containing 3–5 wt% aromatic compounds; and

Type 3 – hydrogenated white spirits, in which the aromatic hydrocarbons have been converted to alicyclic hydrocarbons and which have an aromatic content of less than 1 wt%.

A further regulated group of products in the USA consists of a blend of the three types of white spirits to meet a maximum of not more than 8 wt% aromatic compounds.

(i) *Description*: Clear, colourless hydrocarbon solvent
(ii) *Boiling range*: 130–220°C (ASTM D1078, ASTM D850, ASTM D86, DIN 51751, NF M07–002)
(iii) *Density*: 0.750–0.797 at 15°C (ASTM D1298, ASTM D3505, ASTM D4052, ASTM D891, ASTM D1250, DIN 51757, NF T60–101)
(iv) *Refractive index*: 1.41–1.44 at 20°C (ASTM D1218-82, DIN 53169)
(v) *Solubility*: Less than 0.1 wt% in water
(vi) *Viscosity*: 0.74–1.65 cps at 25°C (ASTM D445-83, DIN 51562, DIN 53015)
(vii) *Volatility*: 0.5–< 0.01; relative evaporation rate, *n*-butyl acetate = 1 (ASTM D3539, DIN 53170)
(viii) *Reactivity*: Reacts with strong oxidizing agents
(ix) *Kauri-butanol value*: 29–33 (ASTM D113)
(x) *Aniline point*: 60–75°C (ASTM D611-82, DIN 51775, NF MO7–021)
(xi) *Flash-point*: 25–80°C (ASTM D56, ASTM D93-80, DIN 51755)
(xii) *Colour (with a Saybolt colorimeter)*: +30 (ASTM D156-82, DIN 51411)
(xiii) *Carbon number range*: 7–12

(*c*) *High-boiling aromatic solvents*

High-boiling aromatic solvents are complex mixtures of aromatic hydrocarbons with carbon numbers from 8 to 16 and boiling typically in the range of 160–300°C, with lower boiling components in some formulations. The total concentration of aromatic compounds is usually greater than 80% but can be as high as 99%, with the remaining constituents comprising a mixture of aliphatics within the same boiling range. Type 1 high-boiling aromatic solvents are catalytically reformed, whereas Type 2 are processed by solvent extraction.

(i) *Description*: Clear, colourless hydrocarbon solvent

(ii) *Boiling-range*: 160–300°C (ASTM D1078, ASTM D850, ASTM D86, DIN 51751, NF M07–002)
(iii) *Density*: 0.879–0.999 at 15°C (ASTM D1298, ASTM D3505, ASTM D4052, ASTM D891, ASTM D1250, DIN 51757, NF T60–101)
(iv) *Refractive index*: 1.5–1.6 at 20°C (ASTM D1218–82, DIN 53169)
(v) *Solubility*: Less than 0.1 wt% in water
(vi) *Viscosity*: 0.8–2.6 cps at 25°C (ASTM D445–83, DIN 51562, DIN 53015)
(vii) *Volatility*: 0.21– < 0.01; relative evaporation rate, *n*-butyl acetate = 1 (ASTM D3539, DIN 53170)
(viii) *Reactivity*: Reacts with strong oxidizing agents
(ix) *Kauri-butanol value*: 85–89 (ASTM D1133)
(x) *Aniline point*: 12–15°C (ASTM D611–82, DIN 51775, NF MO7–021)
(xi) *Flash-point*: 45–110°C (ASTM D56, ASTM D93–80, DIN 51755)
(xii) *Colour (with a Saybolt colorimeter)*: +30 (ASTM D156–82, DIN 51411)
(xiii) *Carbon number range*: 8–16

1.3 Technical products and impurities

There are five major US producers of special boiling-range solvents, white spirits and high-boiling aromatic solvents. Table 1 presents technical data and specifications for representative solvents from these sources. A similar range of products is available from producers in Europe, Japan and elsewhere.

Detailed analyses were reported for several samples of petroleum solvents used in toxicity studies in the USA (Carpenter *et al.*, 1975a,b,c, 1977). The data are summarized in Table 2.

(*a*) *Special boiling-range solvents*

Trade names: Clairsol; Exxsol DSP; Halpasol; Hydrosol; Indusol; Shellsol; Solfina

Some typical technical grades available in Europe are (SBP is special boiling-point and the numbers refer to boiling range): SBP 40/65, SBP 80/100, SBP 100/140, SBP 40/100, SBP 80/110, SBP 100/160, SBP 60/95, SBP 100/120, SBP 145/160. They may be Types 1, 2 or 3 special boiling range solvents, but the majority available today are of Type 2 (hydrogenated). In the past 20–30 years, there has been a pronounced move from nonhydrogenated grades towards hydrogenated (i.e., minimal aromatics) and low *n*-hexane (less than 5 wt%) grades. Low *n*-hexane grades are produced by distillation and/or blending. Type 1 hydrodesulfurized special boiling range solvents typically contain less than 0.5 wt% benzene; hydrogenated grades (Types 2 and 3) contain less than 0.002 wt% benzene.

According to a large Japanese survey of petroleum distillate solvent samples collected in various parts of the country, the average concentrations of *n*-hexane and benzene in low-boiling samples (corresponding approximately to special boiling-range solvents) were 5.1% v/v (range, 0.0–43%) and 0.8% v/v (range, 0.0–3.5%), respectively (Kasahara *et al.*, 1987). Petroleum ether typically has a high concentration of hexanes containing mainly pentanes and hexanes.

Table 1. Technical data and specifications for representative petroleum solvents from US producers[a]

Solvent	Boiling range (°C)	Flash-point (°C)	Aniline point (°C)	Kauri-butanol value	Composition (vol%)			
					Paraffins (aliphatics)	Naphthenes (alicyclics)	Aromatics	Olefins
Special boiling-range solvents								
Petroleum ether	38–60	<–18	61	26	81	17	2	–
Rubber solvent	40–135	–	60	35	66	33	2	–
	42–137	<–18	60	34	82	14	4	–
	42–138	<–18	57	35	65	31	4	0.2
	44–132	<–18	55	32	84	14	2	–
	64–114	<–18	57	34	80	12	9	0.1
VM & P naphtha	118–138	7	52	39	52	37	11	–
	118–149	10	56	56	69	15	15	–
	118–144	10	61	36	79	12	9	–
	119–129	13	54	38	49	42	10	–
	119–130	13	52	39	47	41	13	–
VM & P naphtha	119–137	11	67	32	57	41	2	0.3
Special naphtholite	121–148	12	56	39	43	49	8	–
	122–139	13	56	46	30	64	6	0.1
Low odour	127–142	18	62	35	42	58	<1	–
White spirits/mineral spirits								
Mineral spirits (low odour)	149–204	41	71	29	56	37	7	–
	154–193	39	62	39	48	46	6	–
	156–199	40	62	35	37	60	2	–
	157–196	41	68	31	57	41	2	0.2
	162–193	44	66	33	50	47	4	–
	179–197	53	84	27	86	14	<1	–

Table 1 (contd)

Solvent	Boiling range (°C)	Flash-point (°C)	Aniline point (°C)	Kauri-butanol value	Composition (vol%)			
					Paraffins (aliphatics)	Naphthenes (alicyclics)	Aromatics	Olefins
Stoddard solvent	144–196	35	55	37	42	47	11	0.2
	149–204	38	63	32	67	20	13	-
	153–198	42	56	37	48	37	15	-
	157–196	41	60	36	54	36	10	0.3
	164–195	44	45	43	23	56	21	-
	166–191	46	59	35	46	40	14	-
Stoddard solvent (low odour)	159–197	42	68	33	47	53	< 1	-
	159–203	40	66	32	48	45	7	-
140 Flash solvent	182–210	59	73	28	75	19	5	-
	183–199	60	71	31	60	37	3	0.3
	186–208	61	64	33	38	60	3	-
	187–209	60	63	33	55	39	7	-
	190–203	64	72	31	45	55	< 1	-
High-boiling aromatic solvents								
A-100	155–173	43	13	92	2	-	98	-
	157–177	43	13	90	1	-	99	-
A-150	182–204	60	16	90	< 1	< 1	99	-
	183–210	66	16	92	2	-	98	-

[a]From National Paint and Coatings Association (1984)

Table 2. Chemical composition of some petroleum solvents (in vol%)[a]

Compound	Rubber solvent[b]	VM & P naphtha[b]	Stoddard solvent[c]	High-boiling aromatic solvent
Paraffins (aliphatics)	41.5	55.4	47.7	0.3[d]
C_5	0.3	trace	–	
C_6	17.8	0.3	–	
C_7	23.4	4.0	–	
C_8	–	21.7	0.9	
C_9	–	18.8	9.5	
C_{10}	–	9.1	20.6	
C_{11}	–	1.5	13.3	
C_{12}	–	–	3.4	
Naphthenes (alicyclics)	53.6	32.7	37.6	0.8[e]
Monocycloparaffins	53.6	30.3	26.0	0.2
C_6	23.2	0.5	–	
C_7	30.4	7.5	2.4	
C_8	–	13.2	4.3	
C_9	–	6.5	5.0	
C_{10}	–	2.2	8.4	
C_{11}	–	0.4	4.9	
C_{12}	–	–	1.0	
Dicycloparaffins	–	2.4	11.6	
C_9	–	1.3	2.7	
C_{10}	–	1.1	4.7	
C_{11}	–	–	3.2	
C_{12}	–	–	1.0	
Aromatics	4.9	11.9	14.7	98.9
Benzene	1.5	0.1	0.1	
Alkylbenzenes	3.4	11.7	14.1	87.5
C_7	3.3	1.6	0.4	
C_8	0.1	5.9	1.4	0.7
C_9	–	3.7	7.6	11.7
C_{10}	–	0.5	3.7	56.2
C_{11}	–	–	0.9	17.3
C_{12}	–	–	0.1	1.5
C_{13}	–	–	–	0.1
Naphthalenes	–	–	–	0.2
Indans and tetralins	–	0.1	0.5	9.2

[a] From Carpenter *et al.* (1975a,b,c, 1977)
[b] Special boiling range solvents
[c] White spirits
[d] C_8 to C_{13}
[e] 0.2% monocyclic, 0.5% di- and tricyclic

(*b*) *White spirits*

Trade names: B.A.S.; C.A.S.; Dilutine; Exxsol D; Halpasol; Hydrosol; Indusol; Sangajol; Shellsol D; Solfina; Solnap; Spirdane; Tetrasol; Varsol

Table 3 lists some of the requirements of specifications for white spirits in France, the Federal Republic of Germany, the UK and the USA and of the International Standards Organization.

The US specification ASTM D235-83 lists the physical and chemical properties of four types of 'mineral spirits'; that shown in the table corresponds to what is generally regarded in Europe as 'white spirits'. Requirements for this grade are also detailed in US Federal Specification P-D-860, Type 1. It generally has a lower aromatic content (1-8%) than European white spirits and less than 0.1 wt% benzene (upper limit). Type 2 (solvent extracted) white spirits contain 3-5 wt% aromatic compounds and less than 0.02 wt% benzene (upper limit). Type 3 (hydrogenated) white spirits must contain less than 0.002 wt% benzene (upper limit). The Federal Republic of Germany's specification, DIN 51632, which also covers requirements for aviation gasoline and turbine fuels, does not specify the level of total aromatic compounds but sets limits on specific aromatic compounds such as toluene and ethylbenzene.

According to a large Japanese survey of petroleum distillate solvent samples, the concentrations of *n*-hexane and benzene in solvents boiling in the range of white spirits were both on average 0.01% v/v (range, 0-0.1% v/v) (Kasahara *et al*., 1987).

Sulfur levels in all three types of white spirits are in general less than 10 mg/kg (ASTM D1266), although levels in Type 2 (solvent extracted) may be up to approximately 200 mg/kg (depending on the degree of hydrodesulfurization).

In general, three principal technical grades of each of the three types of white spirits are available, as follows: 'low flash' grades (flash-point, 25-30°C; boiling range, 130-160°C); 'regular flash' grades (flash-point, 40-50°C; boiling range, 150-190°C); and 'high flash' grades (flash-point, 60-70°C; boiling range, 190-220°C). These grades are available throughout Europe.

(*c*) *High-boiling aromatic solvents*

Trade names: A-100; A-150; Caromax; Hydrosol; Indusol; Shellsol; Solvantar; Solvarex; Solvesso

The three main technical grades of high-boiling aromatic solvents that are available on the western European market are fractions boiling at 160-180°C, 180-200°C and 220-290°C. The sulfur content of these grades is generally less than 10 mg/kg, although the sulfur content of Type 2 (solvent extracted) high-boiling aromatic solvents may reach up to several hundred milligrams per kilogram. The benzene content is less than 0.02 wt% (upper limit). The 1,3,5-trimethylbenzene (mesitylene) content of a high-boiling aromatic solvent boiling in the range of 160-180°C can be up to 10 wt%.

Table 3. Specifications for white spirits in selected countries and internationally

Country, product and specification reference	Distillation IBP/FBP[a] (°C)	Flash-point (°C)	Kauri-butanol value (min/ max)	Sulfur content (wt%)	Colour (Saybolt)	Aromatic content
Germany, Federal Republic of						
Testbenzine (white spirits) (DIN 51632)	130 min/ 220 max	21 min	-	-	+20 max (Hazen colour number)	-
UK						
Mineral solvents (white spirits, type A) (BS 245:1976)	Approx. 130/ 220 max	Above 32	-	-	Not darker than standard colour solution	<25% v/v
Mineral solvents (white spirits, type B) (BS 245:1976)	Approx. 130/ 220 max	Above 32	-	-	Not darker than standard colour solution	25–50% v/v
USA						
Mineral spirits type 1 – regular (Stoddard solution) (ASTM D235-83)[b]	149 min/ 208 max	38 min	29/45	–[c]	+25 min	-
International standard						
Mineral solvents for paint – white spirits, etc. (ISO 1250)		(technically identical to BS 245:1976)				

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[a] IBP, initial boiling-point; FBP, final boiling-point

[b] Also includes specifications for high flash-point (60°C min), odourless (Kauri-butanol value, 29 max) and low dry-point (185 max) types of mineral spirits

[c] Bromine number, max 5

2.1 Production and use

(*a*) *Production*

Table 4 presents US production of seven solvent products in 1985. Estimated production of all special boiling-range solvents was 2.5 million tonnes, of which 322 000 tonnes were used in paints and coatings. Table 5 presents total sales and the quantities estimated to have been used in the paints and coatings industry for three major products. Approximately 75% of the aliphatic solvents used in paints and coatings are white spirits (SRI International, 1986).

Table 4. US production of seven solvent products in 1985 (thousands of tonnes)[a]

Solvent	Production
Special boiling-range solvents	
Rubber solvent	54.0
VM & P naphtha	151.2
White spirits	
Odourless white spirits	236.0
White spirits (Stoddard solvent)	324.0
140 Flash solvent	362.1
High-boiling aromatic solvents	
A-100	118.4
A-150	171.5

[a] Data provided by Tracor Technology Resources, Inc.

(i) *Special boiling-range solvents*

In general, special boiling-range solvents are produced in petroleum refineries. Figure 2 is a simplified flow scheme for the production of hydrogenated special boiling-range solvents (Type 2). Naphtha fractions from the atmospheric distillation of crude oil (light and full-range straight-run naphthas) are first subjected to hydrodesulfurization, defined as mild treatment with hydrogen in the presence of a catalyst in order to remove sulfur, followed by hydrogenation, which is treatment with hydrogen in the presence of a different catalyst. Typically, pressures of 19.7–98.7 atm and temperatures of 200–350°C are used in the hydrogenation of these products.

The hydrogenation step converts most of the aromatic hydrocarbons into alicyclic hydrocarbons, leaving less than 0.02 wt% total aromatic content and less than 0.002 wt% benzene. Alternatively, aromatics can be removed by solvent extraction. After hydrogenation, the solvent stream undergoes fractional distillation into narrow and wide boiling ranges, such as SBP 40/65 and SBP 100/160. The sequence of hydrogenation and distillation can be reversed. For the production of hydrodesulfurized special boiling-range solvents (Type 1),

Table 5. US sales and quantities used in the paints and coatings industry (PCI) of three solvents (thousands of tonnes)[a]

Year	Mineral spirits		VM & P naphthas		Lacquer diluents	
	Total	PCI	Total	PCI	PCI	Total
1973	1134	454	211	116	145	91
1974	1061	426	211	111	140	86
1975	1029	370	206	98	125	66
1976	943	372	197	98	126	68
1977	893	372	183	91	118	70
1978	862	374	177	88	116	70
1979	841	363	175	86	113	68
1980	771	331	150	70	91	54
1981	746	320	132	63	86	50
1982	701	302	116	54	68	39
1983	717	315	127	61	79	45
1984	721	320	134	63	79	45
1985	717	324	141	66	75	43

[a] From SRI International (1986)

fractional distillation occurs immediately after hydrodesulfurization, and no hydrogenation step is performed. Type 3 special boiling-range solvents are produced by simple tank blending with an appropriate aromatic product.

(ii) *White spirits*

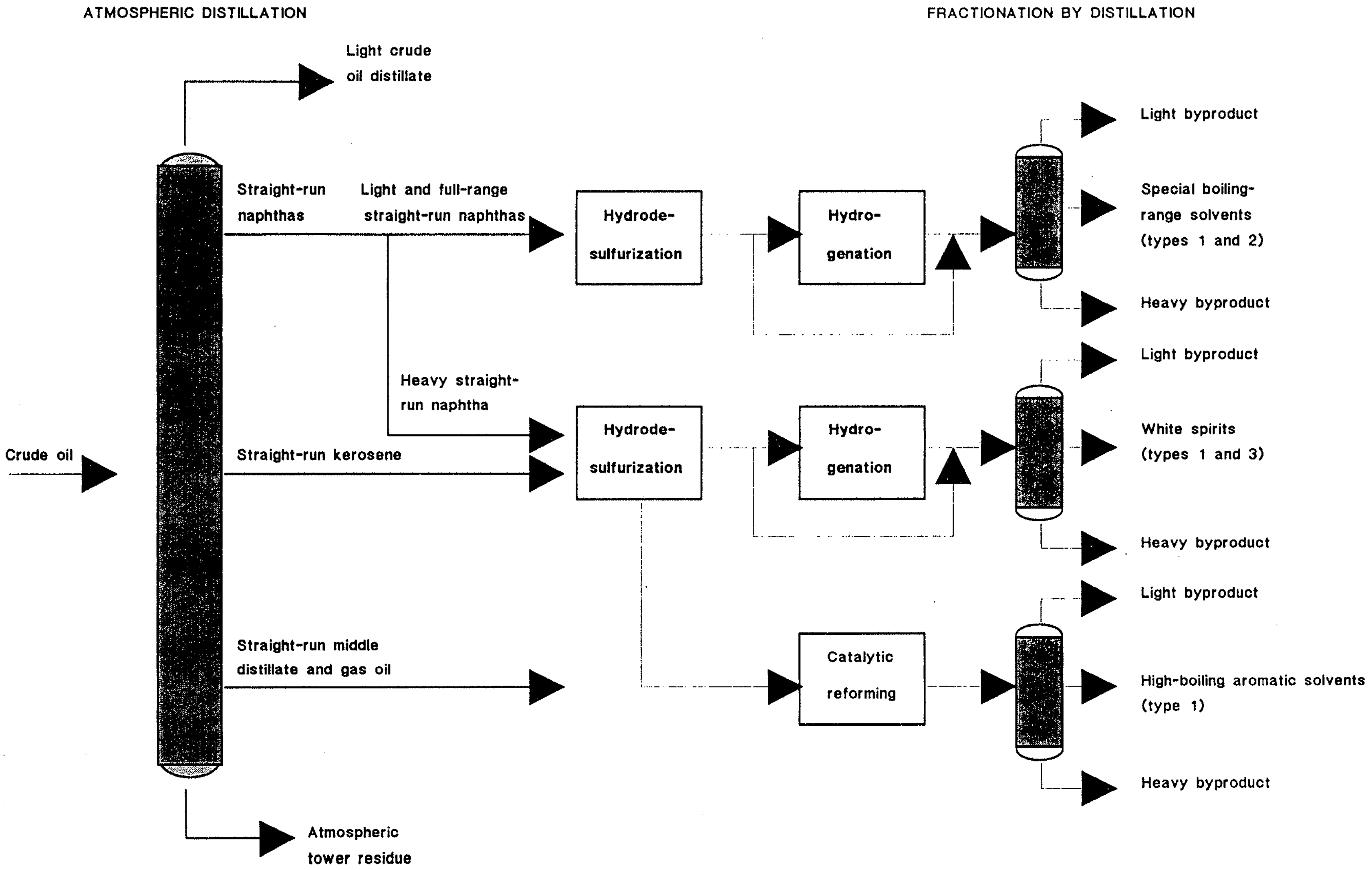
White spirits are also produced in petroleum refineries. Figure 2 includes a simplified flow scheme for the production of Type 1 (hydrodesulfurized) and Type 3 (hydrogenated) white spirits. The heavy straight-run naphtha and straight-run kerosene fractions from the atmospheric distillation of crude oil are first subjected to hydrodesulfurization, followed by fractional distillation into the appropriate boiling ranges to produce Type 1 white spirits. The sequence of hydrodesulfurization and distillation may be reversed. Type 1 white spirits are hydrogenated to produce Type 3. Hydrogenation reduces the total aromatic hydrocarbon content to less than 1 wt% and benzene to less than 0.002 wt%. The sequence of hydrogenation and distillation may be reversed. In the USA, Type 3 'odourless' white spirits are usually derived from alkylation process streams and are principally isoparaffins.

Type 2 white spirits are produced by extracting kerosene-range feedstock with sulfolane, sulfur dioxide and *N*-methylpyrollidone, followed by fractional distillation; hydrodesulfurization may also be carried out.

(iii) *High-boiling aromatic solvents*

High-boiling aromatic solvents are also produced in petroleum refineries (Fig. 2). Heavy straight-run naphtha and straight-run kerosene fractions from the distillation of

Fig. 2. Simplified flow scheme of the production of special boiling–range solvents, white spirits and high–boiling aromatic solvents



crude oil are first subjected to hydrodesulfurization, then the alicyclic molecules in the naphtha are converted into aromatic compounds in a catalytic reformer by treatment at high temperatures and pressures, liberating hydrogen. Fractional distillation then results in the production of different technical grades of Type 1 high-boiling aromatic solvents.

Type 2 products are produced by extracting middle distillate feedstock with sulfolane, sulfur dioxide and *N*-methylpyrollidone followed by fractional distillation.

(*b*) *Use*

(i) *Special boiling range solvents*

Special boiling range solvents are used in a wide range of applications, the principal ones being (approximate percentage of consumption in western Europe): adhesives (34%); paints, lacquers and varnishes (20%); polymerization reaction diluents (10%); rubber industry (11%); and gravure inks and other miscellaneous applications (25%). The aliphatic solvents are used extensively in alkyd resin systems in paints and coatings, as well as for linseed oil and oleoresin varnishes and in nonaqueous dispersion coating systems. These uses are the principal ones worldwide, although the percentages used in the different applications may vary somewhat with geographic region.

Table 6 gives estimated consumption of special boiling range solvents in western Europe in 1972 and 1986. There has been a major shift from special boiling range solvents containing aromatic compounds to those which have been hydrogenated and have a minimal aromatic content, for technical reasons and as a result of concern about human health and the environment. There has also been a move away from products containing high levels of *n*-hexane to those containing less than 5 wt%, also in relation to health effects (SRI International, 1986).

Table 6. Consumption of petroleum solvents in western Europe (thousands of tonnes)

Solvent	1972	1986
Special boiling-range solvents		
Type 1 and 3 (containing aromatics)	180	40
Type 2 (hydrogenated)	90	210
Total	270	250
White spirits		
Type 1 (hydrodesulfurized)	670	540
Type 2 (solvent extracted)	30	40
Type 3 (hydrogenated)	50	120
Total	750	700
High-boiling aromatic solvents		
Type 1 (catalytically reformed)	160	264
Type 2 (solvent extracted)	40	66
Total	200	330

(ii) *White spirits*

The principal uses for white spirits in western Europe (approximate percentage of consumption) are as follows: paints, lacquers and varnishes (60%); degreasing/industrial cleaning (9%); wood treatment (4%); chemical processes (3%); household, cosmetic and toiletries (3%); and miscellaneous (21%).

Table 6 gives estimated consumption of white spirits in western Europe. There has been a move towards the use of hydrogenated white spirits over the last decade, owing to their reduced odour and for technical reasons. Hydrogenation facilities were first introduced in the mid-1960s, and capacity has been increasing steadily since.

(iii) *High-boiling aromatic solvents*

High-boiling aromatic solvents are used principally in: paints, lacquers and varnishes (58%); agrochemicals (16%); industrial cleaning/degreasing (9%); chemical processes (3%); and miscellaneous (inks, plastisols, lubricant additives, oil field chemicals) (14%). Table 6 also gives estimated western European consumption of these solvents.

(c) *Regulatory status and guidelines*

The US Food and Drug Administration (1988) permits the use of petroleum naphtha in foods if it is a mixture of liquid hydrocarbons, essentially paraffinic and naphthenic in nature, obtained from petroleum and is refined to have a boiling range of 80–150°C and a nonvolatile residue content of 0.002 g/100 ml max and to meet specified ultraviolet absorbance limits.

Examples of occupational exposure limits for petroleum solvents in 12 countries are presented in Table 7.

Table 7. Occupational exposure limits for petroleum solvents[a]

Solvent[b]		Country	Year	Concentration		Interpretation[c]
				ppm	mg/m^3	
Petroleum ether		Switzerland	1985	500	2000	TWA
Rubber solvent (naphtha)		Belgium	1984	400	1600	TWA
		Mexico	1985	400	1600	TWA
		Netherlands	1986	400	1600	TWA
		USA (ACGIH)	1988	400	1600	TWA
		Venezuela	1985	400	1600	TWA
VM & P naphtha		Mexico	1985	300	1350	TWA
[CAS No. 8032-32-4]		USA (ACGIH)	1988	300	1350	TWA
White spirits						
Aromaticity	*Boiling range*					
<1%	60–90°C	Finland	1987		350	TWA
					450	STEL
<1%	80–110°C				1200	TWA
					1600	STEL

Table 7 (contd)

Solvent[b]	Country	Year	Concentration		Interpretation[c]
			ppm	mg/m³	
<1% >110°C	Finland (contd)			900	TWA
				1200	STEL
>20% >110°C				770	TWA
				1020	STEL
100% >110°C				240	TWA
				360	STEL
Aromaticity					
<10%	Norway	1981	200	1050	TWA
>10%, <20%			100	575	TWA
>20%			25	120	TWA
	Sweden	1987	~85	500	TWA
			~110	625	STEL
	UK	1987	100	575	TWA
			125	720	STEL (10-min)
	USSR	1984		300	TWA
Stoddard solvent	Belgium	1984	100	575	TWA
	Chile	1985	80	460	TWA
	Mexico	1985	500	2950	TWA
	Netherlands	1986	100	575	TWA
	Switzerland	1984	100	580	
	USA (OSHA)	1985	500	2950	TWA
	(NIOSH)	1986		350	
				1800	Ceiling (15-min)
[CAS No. 8052-41-3]	(ACGIH)	1988	100	525	TWA
	Venezuela	1985	100	575	TWA
			150	720	Ceiling
Solvent naphtha (as carbon)	USSR	1986		100	TWA

[a] From Direktoratet for Arbeidstilsynet (1981); International Labour Office (1984); Arbeidsinspectie (1986); Institut National de Recherche et de Sécurité (1986); National Institute for Occupational Safety and Health (1986); Cook (1987); Health and Safety Executive (1987); National Swedish Board of Occupational Safety and Health (1987); Työsuojeluhallitus (1987); American Conference of Governmental Hygienists (1988)

[b] OSHA, Occupational Safety and Hygiene Administration; NIOSH, National Insitute for Occupational Safety and Health; ACGIH, American Conference of Governmental Hygienists

[c] TWA, time-weighted average; STEL, short-term exposure limit

2.2 Occurrence

(*a*) *Natural occurrence*

Petroleum-derived solvents do not occur naturally in the environment, but only as components of the crude oils from which they are derived (International Programme on Chemical Safety, 1982).

(*b*) *Occupational exposure*

On the basis of one National Occupational Hazard Survey, the US National Institute for Occupational Safety and Health (1974) has estimated that 3500 workers were potentially exposed to petroleum ether (as ligroin [CAS No. 8032-32-4]; a special boiling range solvent) in the USA in 1972–74; 26 400 workers were potentially exposed to rubber solvent. According to a National Occupational Exposure Survey (National Institute for Occupational Safety and Health, 1983), 327 000 workers were potentially exposed to varnish makers' and painters' naphtha (a special boiling range solvent), 160 000 to white spirits and 521 800 to Stoddard solvent in the USA in 1981–83.

Occupational exposure levels have been measured for a wide range of petroleum solvents. The following paragraphs present data available for the types of solvents covered in this monograph.

In a US plant that used a contact adhesive containing rubber solvent and toluene to assemble rubber life rafts, personal time-weighted average (TWA) exposures to rubber solvent ranged from 5 to 12 ppm with an average of 9 ppm (Apol, 1981).

Levels of naphtha have been reported in a variety of US manufacturing plants. In a plant where baseball bats were manufactured, breathing zone levels were 13–190 ppm (mean, 78 ppm; Rivera & Rostand, 1975). During the installation of plastic laminates to kitchen and bathroom counter tops, levels of naphtha were 363–3158 mg/m^3 (mean, 1113 mg/m^3; Apol, 1980). In the printing industry, air levels of naphtha in personal breathing samples from off-set printers were 94–258.4 mg/m^3 (mean, 140.4 mg/m^3; Gorman, 1982); levels of varnish makers' and painters' naphtha to which lithographers were exposed were 58–242 mg/m^3 (mean, 122.1 mg/m^3; Chrostek *et al.*, 1979). In another study, levels of petroleum naphtha in breathing zones and in the general air in the printing industry were 18–106 (average, 53) mg/m^3 (Gunter, 1986). Ambient indoor air area levels of naphtha in a large US Federal office building were 8.4–22.7 mg/m^3 (Watanabe & Love, 1980). In two shoe manufacturing plants, TWA area concentrations of naphtha were 10–162 mg/m^3 (mean, 59 mg/m^3) and those of aliphatic naphtha, 19–522 mg/m^3 (mean, 305 mg/m^3; Tharr *et al.*, 1982). In a plant that used petroleum naphtha as a release agent in the manufacture of refrigerators, levels were 15–147 mg/m^3 (Markel & Shama, 1974), and in a plant where window assemblies for cars were manufactured, TWA levels of naphtha were 32–191 mg/m^3 (mean, 79 mg/m^3; Lucas, 1981).

In a US factory where white spirits were used to clean silk screens, air levels were 137–385 mg/m^3 in personal samples and 149–336 mg/m^3 in area samples (Geissert, 1975). In a US factory manufacturing naval catapults, exposure to white spirits ranged from < 1 to 2615 mg/m^3, with an average of 208 mg/m^3 (Gilles, 1975). In a US plant in which white spirits were used to clean automobile starters and generators, the TWA in personal air samples was 43–594 mg/m^3, with an average of 275 mg/m^3; at the 'Kleen Abrader' (a vibrating machine containing white spirits and abrasive stone pellets), a value of 3967 mg/m^3 was found (Levy, 1975). At a US plant manufacturing vinyl floor coverings in which white spirits were used in the solvent/wax solution, personal TWA levels in air were 0.3–8 ppm, with an average of 4.1 ppm (Belanger & Elesh, 1979). Air concentrations of white spirits in the breathing zone of telephone wire splicers, who used it to dissolve petroleum jelly for filling telephone cables, were 79–244 mg/m^3, with an average of 144 mg/m^3 (Gunter, 1980). At a US tool manufacturing plant, the 8-h TWA exposures of tool repair technicians in 1986 were 20–95 mg/m^3 in personal samples, with a mean of 55 mg/m^3, and 58–266 mg/m^3 (mean, 116 mg/m^3) in process air samples (Blade, 1987).

Personal exposures to Stoddard solvent in the press room of two US daily newspapers were 13–319 mg/m^3 (average, 83 mg/m^3; Hollett *et al.*, 1976) and 5–9 mg/m^3 (average, 7 mg/m^3; Kronoveter 1977); those in a US printing facility were 0.1–16 mg/m^3 (Gunter, 1982). Breathing zone samples taken at a commercial airline maintenance hanger showed concentrations of Stoddard solvent ranging from 363 to 8860 mg/m^3, with an average of 3000 mg/m^3 (Gunter, 1975a). A US manufacturer of ski boots reported levels of 345–451 mg/m^3 Stoddard solvent in the boot finishing and polishing department (Gunter, 1975b). In the dry-cleaning industry, 8-h TWA concentrations of Stoddard solvent were 15–35 ppm (Oberg, 1968). During automobile washing in Finland, TWA concentrations of Stoddard solvent were 5–465 mg/m^3 in personal samples and 15–390 mg/m^3 in area samples. For heavy vehicles, the corresponding values were 45–805 and 40–685 mg/m^3, respectively (Niemelä *et al.*, 1987).

Exposure to petroleum solvents during the manufacture and application of paint products is described in the monograph on occupational exposures in paint manufacture and painting (see p. 329).

(*c*) *Air*

Because of their low solubility in water and their relatively high volatility, petroleum solvents are found principally in the air after their release. They may undergo photodegradation in the atmosphere.

2.3 Analysis

For petroleum solvents with final boiling-points up to about 100°C, all of the hydrocarbon components present can be identified and quantified using high-resolution capillary column gas chromatography. For products with a higher final boiling-point, it is difficult to identify all of the components, and analysis is usually for total aliphatic, alicyclic and aromatic hydrocarbons.

A multicolumn gas chromatograph has been designed to separate aromatic, alicyclic and aliphatic components in hydrocarbon solvents that boil at up to 200°C. It consists of three columns – a polar, a nonpolar and a molecular sieve. The first is used to separate aromatic compounds from saturated compounds, the second is used to separate aromatic compounds by boiling-point, and the third to separate alicyclic comounds from aliphatic compounds by carbon number.

Ultraviolet spectrometry can be used to estimate the total aromatic content (ASTM D1019). Sulfur levels are determined by microcoulometry (ASTM D1266).

The total hydrocarbon concentration of various petroleum solvents can be determined in air using a method based on charcoal tube sampling and gas chromatography with flame ionization detection. The working range is 100–2000 mg/m^3 for a 5-l air sample (Eller, 1984).

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

3.1 Carcinogenicity studies in animals

Inhalation

Rat: Groups of 50 male and 50 female Wistar rats, eight to nine weeks of age, were exposed by inhalation to 0 (controls), 470 ± 29, 970 ± 70 or 1830 ± 130 mg/m^3 of a high-boiling aromatic solvent (high-flash aromatic naphtha; ASTM-3734; a 50:50 blend of Shellsol A and Solvesso) containing 13 major components (predominantly C_9 aromatic compounds)[1]. Exposure was for 6 h per day on five days per week for up to 12 months. Ten males and ten females from each group were killed after six months, 25 males and 25 females from each group after 12 months and the remaining animals four months after the end of exposure. A single mammary adenocarcinoma was found in a female in the high-dose group killed at six months. In rats killed at 12 months, there was a glioblastoma in the brain in a low-dose male, a splenic lymphoma in a high-dose male and a leiomyoma of the uterus in a high-dose female (Clark & Bird, 1989). [The Working Group noted the short duration of the study, and the absence of pathological examination of the surviving rats from each group killed at 16 months.]

3.2 Other relevant data

(*a*) *Experimental systems*

Absorption, distribution, excretion and metabolism

No data were available to the Working Group.

Toxic effects

The toxicology of petroleum solvents has been reviewed (National Institute for Occupational Safety and Health, 1977; International Programme on Chemical Safety, 1982). A summary of the acute toxicities of mixtures of aromatic and saturated hydrocarbons representing the types of commercial solvents is available (Hine & Zuidema, 1970).

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[1] *ortho*-Xylene, 2.27%; *n*-propylbenzene, 4.05%; 1-methyl-3-ethylbenzene, 7.14%; 1-methyl-4-ethylbenzene, 16.60%; 1,3,5-trimethylbenzene, 9.35%; 1-methyl-2-ethylbenzene, 7.22%; 1,2,4-trimethylbenzene, 32.70%; 1,2,3-trimethylbenzene, 2.76%; 1-methyl-3-*n*-propylbenzene and 1,2-diethylbenzene, 6.54%; 1-ethyl 3,5-dimethylbenzene, 1.77%; no benzene detected; nonaromatic compounds, 0.46%

Acute oral and inhalation toxicities in rats and percutaneous toxicity in rabbits are shown in Table 8. Toxicity was more pronounced with samples containing higher levels of aromatic compounds than with virtually aromatic free products. The irritating potential of the mixtures for skin and eye (evaluated according to the method of Draize in albino rabbits) ranged from minimally to moderately irritating (Hine & Zuidema, 1970).

(i) *Special boiling range solvents*

A hexane-containing and a heptane-containing petroleum solvent fraction had low toxicity (Table 8). Irritation of the skin was slight and eye irritation minimal, and there was practically no percutaneous toxicity in rabbits (Hine & Zuidema, 1970).

Rats were exposed to either 200 or 500 ppm *n*-hexane or to petroleum benzine vapour [assumed boiling range, 30–150 °C] containing 200 or 500 ppm *n*-hexane for 12 h per day for 24 weeks. Peripheral nerve function was clearly impaired by 500 ppm *n*-hexane, slightly impaired by 200 ppm *n*-hexane and by petroleum benzine vapour containing 500 ppm *n*-hexane, and impaired even less by petroleum benzine containing 200 ppm *n*-hexane. The authors concluded that other components of petroleum benzine might inhibit the neurotoxicity of *n*-hexane (Ono *et al.*, 1982).

The inhalation toxicity of a rubber solvent (boiling range, 76–111 °C; composition (in vol%): paraffins, 41; monocycloparaffins (naphthenes), 54; benzene, 1.5; alkyl benzenes, 3.4; monoolefins, 0.1) was studied in mice, rats, cats and beagle dogs. Animals were exposed to concentrations of 480–63 000 ppm. Acute exposure to high concentrations resulted in loss of motor coordination and central nervous system depression. Eye irritation was described in rats (at 9600 ppm for 4 h), toxic stress in dogs (3200–6200 ppm, 4 h) and respiratory rate depression in mice (63 000 ppm). A 4-h LC_{50} of 15 000 ppm was estimated for rats. No significant toxic effect was noted in rats or in beagle dogs exposed subacutely to up to 2000 ppm rubber solvent for 6 h per day on five days per week for 13 weeks (Carpenter *et al.*, 1975c).

The inhalation toxicity of a varnish makers' and painters' naphtha (boiling range, 118–150 °C; composition (in vol%): paraffins, 55; monocycloparaffins, 30; dicycloparaffins, 2.5; alkylbenzenes, 12; benzene, 0.1) was also studied in mice, rats, cats and beagle dogs. Animals were exposed to concentrations of 280–15 000 ppm. Acute exposure to high concentrations resulted in loss of motor coordination and central nervous system depression. Eye irritation was described in rats (3400 ppm, 4 h) and dogs (3400 ppm, 2 h) and respiration rate was decreased in mice (> 2600 ppm, 1 min). A 4-h LC_{50} of 3400 ppm was estimated for rats. No significant toxic effect was noted in rats or in beagle dogs exposed subacutely to up to 1200 ppm for 6 h per day on five days per week for 13 weeks (Carpenter *et al.*, 1975a).

(ii) *White spirits*

The effects of a paint thinner (boiling range, 140–190 °C) were reported in rats, guinea-pigs, rabbits, beagle dogs and squirrel monkeys. The samples were a complex mixture of 80–86% saturated hydrocarbons, 1% olefins and 13–19% aromatic compounds. Animals were exposed for 8 h a day on five days per week for 30 exposures or continuously (23.5 h per day on seven days per week) for 90 days. In the continuous 90-day experiment (exposure concentrations, 114–1270 mg/m^3), increased mortality occurred only among guinea-pigs exposed to 363 mg/m^3 or more. Gross examination revealed irritation and congestion of the

Table 8. Acute toxicities of mixtures of aromatic and saturated hydrocarbons representing the three types of commercial solvents[a]

Solvent type (boiling range; °C)	Principal components	Oral LD_{50} (ml/kg bw; rats)[b]	Inhalation 4-h LC_{50} (ppm; rats)	Aspiration mortality (rats)	Percutaneous 4-h LD_{50} (mg/kg bw; rabbits)
Special boiling range solvents					
65–75	C_6 normal and isoparaffins (hexanes) and naphthenes (cyclohexane, methylcyclopentane)	>25	73 680 (66 310–79 940)		>5.0
91–104	C_7 normal and isoparaffins (heptanes) and naphthenes (methylcyclohexane, dimethylcyclopentane)	>25	14 000–16 000		>5.0
White spirits					
156–180	C_9 and C_{10} normal and isoparaffins and naphthenes	>25	2000–2600		>5.0
187–212	C_{11} and C_{12} normal and isoparaffins and naphthenes	>25	>710[c]		~5.0
174–216	C_{12} isoparaffins	>25	>792[c]		>5.0
195–260	C_{13} to C_{16} normal and isoparaffins and naphthenes	>25	>263[c]	5/10	>5.0
High-boiling aromatic solvents					
138–141	C_8 aromatics (*ortho*–, *meta*– and *para*-xylene; ethyl benzene)	10.0 (7.5–13.3)	6350 (4670–8640)		~5.0
163–203	C_9, C_{10} and C_{11} aromatics	4.5 (3.0–6.8)	>2450[c]		~5.0
188–209	C_{10} and C_{11} aromatics	13.3 (7.5–23.7)	>580[c]		~5.0
196–264	C_{11} to C_{14} aromatics	12.3 (8.1–18.7)	>553[c]	5/10	~5.0

[a] From Hine & Zuidema (1970)

[b] Doses above 25 ml/kg bw not practical for testing

[c] Maximum concentration attainable at 25°C

lungs in all species, and the severity of lung irritation and the number of animals involved appeared to be dose related. In the 30-day experiment, the only signs of toxicity were seen in guinea-pigs exposed to the highest concentration (1353 mg/m^3), which had lung irritation, congestion and emphysema on histopathological examination (Rector *et al.*, 1966).

The inhalation toxicity of a Stoddard solvent (boiling range, 153-194 °C; composition (in vol%): paraffins, 48; mono- and dicycloparaffins, 26 and 12; alkylbenzenes, 14; benzene, 0.1) was studied in mice, rats, cats and beagle dogs. Animals were exposed to 84–1700 ppm of the solvent for up to 13 weeks. Marked tubular regeneration of the kidneys, which may be indicative of solvent-induced kidney damage, was detected at sacrifice in male rats exposed to 190 or 330 ppm for 13 weeks. Eye irritation and blood around the nostrils was described in rats exposed to 1400 ppm for 8 h. Central nervous system depression was seen in all species at higher exposure concentrations. Depressed respiration rate was observed in mice exposed to 1700 ppm (Carpenter *et al.*, 1975b).

Rats were exposed for 4 h per day for four consecutive days to 214 mg/m^3 ($\sim$45 ppm) of white spirits containing mainly C_9–C_{12} hydrocarbons and consisting of approximately 61% paraffins, 20% naphthenes and 19% aromatics (boiling range, 150–195 °C). Irritation of the upper respiratory tract (loss of cilia, mucous and basal-cell hyperplasia, squamous metaplasia) was observed (Riley *et al.*, 1984).

The subchronic inhalation toxicity of dearomatized white spirits (boiling range, 155–193 °C; containing 58% paraffins, 42% naphthenes and $<0.5\%$ aromatics) and of a C_{10}–C_{11} isoparaffin (boiling range, 156–176 °C; 100% isoparaffins) was investigated in rats. Animals were exposed for 6 h per day on five days per week for 12 weeks to concentrations of about 5.6 (900 ppm) and 1.9 g/m^3 (300 ppm) of the two solvents, respectively. The primary effect of both solvents after four weeks of exposure was kidney toxicity in male rats (described as mild tubular toxicity), the incidence and severity of which appeared to increase with increasing exposure concentration and duration. No other significant toxic effect was observed at the levels tested (Phillips & Egan, 1984).

In rats exposed by inhalation to industrial white spirits composed of a 99% C_{10}–C_{12} mixture of branched-chain aliphatic hydrocarbons at to 6500 mg/m^3 for 8 h per day on five days per week for 12 months, increased urinary activity of lactic dehydrogenase (a marker of distal tubular damage) and reduced kidney function were seen (Viau *et al.*, 1984).

(iii) *High-boiling aromatic solvents*

The inhalation toxicity of a high-boiling aromatic solvent (boiling range, 184-206 °C; composition (in vol%): alkylbenzenes, 87.5; naphthalenes, 2; indanes, 9; naphthenes, 0.8; paraffins, 0.3) was studied in rats, cats and beagle dogs. No significant toxicity was observed in any species after exposure to 380 mg/m^3 (66 ppm) for 6 h per day on five days per week for 13 weeks. An 8-h exposure of rats to 8700 mg/m^3 of an aerosol of the solvent resulted in early nasal and occular irritation followed by progressive loss of coordination and the death of 2/10 animals (Carpenter *et al.*, 1977).

The inhalation toxicity of the high-boiling aromatic naphtha tested for carcinogenicity (see section 3.1) was investigated in rats. The animals were exposed to 0, 450, 900 or 1800 mg/m^3 of the solvent for 6 h per day on five days per week for up to 12 months. Reductions in body weight gain were observed in males exposed to the highest dose over the first four weeks and in female rats exposed to the two higher concentrations over the first four or 12 weeks. In males exposed to the highest dose, liver and kidney weights were increased at six and 12 months. Various statistically significant haematological changes were observed transiently in male rats up to six months, but were not considered to be of biological relevance by the authors. A preliminary 13-week inhalation study with Shellsol A resulted in increases in liver and kidney weights in rats exposed to 7400 and 3700 mg/m^3, and in a low-grade anaemia in rats at 7400, 3700 and 1800 mg/m^3 (Clark & Bird, 1989).

Effects on reproduction and prenatal toxicity

As reported in an abstract, female CD rats [number of animals unspecified] were exposed by inhalation for 6 h per day to either commercial white spirits (100 or 300 ppm) or C_8–C_9 isoparaffinic hydrocarbon solvents (400 or 1200 ppm) on days 6–15 of gestation. No maternal effect was reported. Fetuses were examined at term for visceral and skeletal development. Male fetuses exposed to 100 ppm white spirits were heavier than control fetuses, and the incidence of skeletal variations was significantly increased in the group exposed to 1200 ppm isoparaffin (Phillips & Egan, 1981). [The Working Group noted the lack of experimental details available.]

As reported in an abstract, Wistar rats [number of animals unspecified] were exposed by inhalation for 6 h per day to 237, 482 or 953 ppm white spirits on days 6–15 of gestation, or to 950 ppm on days 3–20 of gestation. Maternal toxicity was reported in the high-exposure groups. Fetuses were examined at term for visceral and skeletal development. No skeletal or visceral anomaly was observed, but significant reductions in fetal weight, delays in skeletal development and extra ribs were reported in the group treated on days 3–20 of gestation (Jakobsen *et al.*, 1986). [The Working Group noted the lack of experimental details available.]

Genetic and related effects[1]

A rubber solvent induced chromosomal aberrations but not sister chromatid exchange in human whole-blood cultures (Altenburg *et al.*, 1979).

As reported in an abstract, C_8–C_9 isoparaffinic hydrocarbon solvents (at 400 and 1200 ppm) did not induce dominant lethal mutations in CD rats exposed for 6 h per day on five days per week for eight consecutive weeks prior to mating (Phillips & Egan, 1981).

Special boiling range spirit 100/140 (a mixture of paraffins and cycloparaffins in the C_5–C_{10} range) was not mutagenic to *Salmonella typhimurium* TA1535, TA1537, TA1538, TA98 or TA100 or to *Escherichia coli* WP2 either in the presence or absence of an exogenous metabolic system from Aroclor-induced rat liver. It did not induce mitotic gene conversion

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[1] Subsequent to the meeting, the Secretariat became aware of a study to investigate the effects of high flash aromatic naphtha in a *Salmonella*/mammalian microsome mutagenicity assay, a hypoxanthine–guanine phosphoribosyl transferase forward mutation assay in Chinese hamster CHO cells, *in-vitro* chromosomal aberration and sister chromatid exchange assays in Chinese hamster CHO cells, and an *in-vivo* chromosomal aberration assay in rat bone marrow (Schreiner *et al.*, 1989).

in *Saccharomyces cerevisiae* strain JD1 or chromosomal aberrations in Chinese hamster ovary cells (Brooks *et al.*, 1988).

A sample of white spirits (boiling range, 160–161 °C; 85% aliphatic compounds, 15% aromatic compounds) was not mutagenic to *S. typhimurium* TA1530, TA1535, TA1537, TA1538, TA98 or TA100 either in the presence or absence of an exogenous metabolic system from Aroclor-induced rat liver. It did not induce sister chromatid exchange in human lymphocytes *in vitro* or chromosomal aberrations *in vivo* in mouse bone-marrow cells (Gochet *et al.*, 1984). As reported in an abstract, white spirits (100 and 300 ppm) did not induce dominant lethal mutations in CE rats exposed for 6 h per day on five days per week for eight consecutive weeks prior to mating (Phillips & Egan, 1981).

As reported in an abstract, Stoddard solvent did not induce mutation in *S. typhimurium* [strain unspecified] or in mouse lymphoma L5178Y TK + /- cells. Neither did it induce chromosomal aberrations in rat bone marrow *in vivo* [details not given] (Lebowitz *et al.*, 1979).

(*b*) *Humans*

Absorption, distribution, excretion and metabolism

White spirits are absorbed through the lungs, and the uptake is enhanced by exercise-induced increase in pulmonary ventilation. Fifteen healthy male volunteers were exposed to 1250 or 2500 mg/m^3 white spirits vapour (boiling-point, 150–200 °C; containing 83% aliphatic and 17% aromatic compounds) either at rest for 30 min (one to four times) or with exercise up to 150 W. Blood levels of *n*-decane and 1,2,4-trimethylbenzene (taken to represent aliphatic and aromatic compounds, respectively) were detected after exposure. The exercise-induced increase was more evident for aromatic compounds than for aliphatic compounds, possibly due to different solubilities in blood (Åstrand *et al.*, 1975). In other studies (Milling Pedersen *et al.*, 1984, 1987) in which volunteers were exposed to 10 ppm (600 mg/m^3) white spirits (99% alkanes [38.7% C_{11}; 44.4% C_{12}] and 1% cycloalkanes [mostly C_{10}]), solvent levels were determined in subcutaneous adipose tissue obtained by biopsy. After 46–48 h, about 50% of the initial concentration of the solvent had disappeared.

Toxic effects

[The Working Group noted that some of the information on the adverse effects of petroleum solvents originates from studies of occupational exposures, which generally involve a complex mixture of various organic solvents and other compounds. Reasons for the variable outcomes include differences in exposure, i.e., type of chemical, intensity and duration. Also, selection bias may have occurred, and the examination methods varied, some possibly being influenced by recent, rather than chronic exposures. Finally, the control groups may not have been appropriate, so that the effect of confounders cannot be ruled out. The reader is referred also to the monograph on occupational exposures in paint manufacture and painting.]

Exposure of volunteers to 2700 mg/m^3 of a Stoddard solvent caused eye irritation (Carpenter *et al.*, 1975b). Opacities in the lens of the eye have been recorded in car painters exposed to a mixture of solvents, including white spirits (Elofsson *et al.*, 1980). Stoddard solvent irritates the skin and may cause contact dermatitis (Nethercott *et al.*, 1980), and petroleum ether applied to the skin may also induce severe irritation (Spruit *et al.*, 1970). Solvents with a high aromatic content are more irritant than those of paraffinic origin in the same boiling range (Klauder & Brill, 1947).

Volunteer painters exposed to 100 ppm white spirits containing 17% aromatic compounds complained of irritation in the upper airways (Cohr *et al.*, 1980). Aspiration of petroleum distillates by fire eaters may induce chemical pneumonitis (Agrawal & Srivastava, 1986).

Petroleum solvents may affect the central nervous system. After acute, intense exposure of 'sniffers', there is first an excitatory phase and later a depressive phase (Prockop, 1979). Volunteers exposed to white spirits at 100–400 ppm for 7 h reported headache, fatigue and incoordination, with dose-associated effects on equilibrium, reaction time, visuo-motoric coordination and memory (Cohr *et al.*, 1980). Exposure to 4000 mg/m^3 white spirits for 0.5 h affected reaction time and short-term memory (Gamberale *et al.*, 1975). Nausea, a sense of intoxication and dizziness have been reported in car painters exposed to white spirits and other solvents (mainly toluene; Husman, 1980).

Subjective symptoms originating from the central nervous system, such as headache, fatigue, poor concentration, emotional instability, impaired memory and other intellectual functions, and impaired psychomotor performance have been reported in a series of cross-sectional studies of paint industry workers, house painters, car painters, shipyard painters and floorlayers, all of whom had been exposed to a mixture of solvents, including petroleum solvents (Hänninen *et al.*, 1976; Hane *et al.*, 1977; Elofsson *et al.*, 1980; Husman, 1980; Anshelm Olson, 1982; Lindström & Wickström, 1983; Cherry *et al.*, 1985; Ekberg *et al.*, 1986). Some of these are short- or mid-term effects, others are potentially persistent. In some studies, dose–response relationships were observed between symptoms and lifetime exposure (duration and intensity) to solvents.

Effects on the peripheral nervous system have been seen in car painters, house painters and shipyard painters who were exposed to a mixture of various organic solvents, including white spirits (Seppäläinen *et al.*, 1978; Elofsson *et al.*, 1980; Husman & Karli, 1980; Cherry *et al.*, 1985; Askergren *et al.*, 1988). However, in house painters, no such effect was observed after an average exposure to 40 cm^3/m^3 white spirits (Seppäläinen & Lindström, 1982).

In workers exposed to a glue solvent (rubber solvent; C_5–C_7 aliphatic and alicyclic hydrocarbons), indications of slight renal tubular effects were reported (Franchini *et al.*, 1983). In another study of car painters exposed to low levels of white spirits and toluene, no such effect was observed (Lauwerys *et al.*, 1985).

Conflicting reports of adverse effects on blood and blood-forming organs were reported in house and car painters exposed to white spirits and other solvents (Hane *et al.*, 1977; Elofsson *et al.*, 1980; Angerer & Wulf, 1985). One case of aplastic anaemia was reported following exposure to Stoddard solvent (Prager & Peters, 1970).

Some indication of effects on muscles (raised serum creatine kinase) has been reported after short-term exposure of volunteers to white spirits (Milling Pedersen & Cohr, 1984).

Effects on fertility and pregnancy outcome

Holmberg (1979) reported a case–control study of 120 children with congenital central nervous system defects and an equal number of matched controls. The cases had been registered with the Finnish Register of Congenital Malformations between June 1976 and May 1978. Four mothers of the children with central nervous system defects, but no control mother, reported having worked with white spirits during the first trimester of pregnancy; two of them had also been exposed to other solvents, such as toluene and xylene. One control mother had been exposed to 'mixed aromatic/aliphatic' solvents.

Holmberg *et al.* (1982) reported a case–control study of 378 children with oral clefts and an equal number of controls. The cases had been registered with the Finnish Register of Congenital Malformations between December 1977 and May 1980. Ten mothers of children with oral clefts and two control mothers reported having worked with lacquer petrol (i.e., white spirits; 85% aliphatics, 15% aromatics) during the first trimester of pregnancy. Four of these case mothers and one control had also been exposed to toluene, xylene, acetates, alcohols, acetone, ethylacetate, dichloromethane, turpentine and fluorotrichloromethane.

[The Working Group noted that in these two studies data on exposure were collected retrospectively, after the malformation had been registered.]

Genetic and related effects

No data were available to the Working Group.

3.3 Epidemiological studies of carcinogenicity in humans

The Working Group chose to address only those papers that specifically reported exposure to 'petroleum solvents', e.g., white spirits, and not those that reported only exposure to 'organic solvents' or to unspecified solvents. Studies in which exposures to toluene, xylene or phenol are mentioned are described in the monographs on those compounds.

Relationships between cancer excesses and exposure to solvents in the rubber industry have been investigated in a number of studies, some of which were evaluated previously (IARC, 1982). Wilcosky *et al.* (1984) performed a case–control study on cases of cancer at five sites in a cohort of 6678 male, hourly-paid, active and retired rubber workers identified in 1964 in the USA (McMichael *et al.*, 1975). Detailed records of potential exposure to 25 specific solvents (data are given for only 20 solvents; Wilcosky *et al.*, 1984) were used to classify jobs, and exposure was evaluated using a set of 70 occupational titles that covered all jobs entailing the same process and materials. These titles were then grouped into heavy, medium and light exposure to solvents, according to assessments by industrial hygienists (McMichael *et al.*, 1975). In white males, exposure to 'specialty naphthas' was associated with an increased relative risk (RR) for lymphosarcoma (1.4; 6 cases) and for lymphatic leukaemia (2.8; 8 cases), and exposure to 'VM & P naphtha' with increased RRs for prostatic cancer (1.6; 4 cases) and for lymphatic leukaemia (2.9; 3 cases). [The Working Group noted that the number of cases in each category is small, multiple exposures were evaluated independently of other exposures, and none of the associations is significant.]

Olsson and Brandt (1980) interviewed 25 men aged 20–65 years admitted consecutively to the Department of Oncology, University Hospital, Lund, Sweden, with a recent diagnosis of Hodgkin's disease. Two controls for each case were selected from the computerized Swedish population register and matched for sex and residence. The cases and controls were interviewed using a questionnaire, and daily exposure to solvents for at least one year more than ten years before diagnosis was recorded for all persons. Twelve of the 25 patients with Hodgkin's disease had been exposed occupationally to organic solvents and six of the 50 controls, giving a RR of 6.6 (95% confidence interval (CI), 1.8–23.8). Two of the cases and none of the controls had been exposed to white spirits.

Hardell *et al.* (1984) performed a case–control study on 102 deceased cases of primary liver cancer in men aged 25–80 years in Sweden; 83 were hepatocellular carcinoma, 15 cholangiocarcinoma, three haemangiosarcomas and one an unspecified sarcoma. For each case, two controls were drawn from the national population register and were matched for sex, age, year of death and municipality. Information about various exposures was obtained by written questionnaires from a close relative of each case and control. Exposure to organic solvents for more than one month was stated by 22.4% of the cases with primary liver cancer and by 13.5% of the controls (RR, 1.8; 95% CI, 0.99–3.4). The RR for cases with hepatocellular carcinoma was 2.1 (95% CI, 1.1–4.0). Most of the cases and controls had been exposed to various types of organic solvents, including thinners, turpentine and white spirits. [The Working Group noted that no stratified analyses were presented for alcohol consumption and solvent exposure, although alcohol consumption was associated with high risk.]

A case–control study of cancer at many sites was performed in Montréal, Canada, to generate hypotheses on potential occupational carcinogens (Siemiatycki *et al.*, 1987a,b). About 20 types of cancer were included, and, for each cancer site analysed, controls were selected from among cases of cancer at other sites. Job histories and information on possible confounders were obtained by interview from 3726 men aged 35–70 years with cancer diagnosed at one of 19 participating hospitals between 1979 and 1985. The response rate was 82%. Each job was translated into a series of potential exposures by a team of chemists and hygienists using a check–list of 300 of the most common occupational exposures in Montréal. Cumulative indices of exposure were estimated for a number of occupational exposures: exposure below the median was considered to be 'nonsubstantial' and that above the median to be 'substantial'. Risks associated with exposure to petroleum–derived liquids were analysed separately. A total of 739 men were classified as having been potentially exposed to 'mineral spirits'. The term 'mineral spirits' included white spirits, Stoddard solvent, VM & P naphtha, rubber solvent, benzine and ligroin (30–90% aliphatics, 1–20% aromatics). Those with long (> 20 years), substantial potential exposure were found to have a RR for squamous–cell cancer of the lung of 1.7 (90% CI, 1.2–2.3), based on 44 cases, and a RR for prostatic cancer of 1.8 (90% CI, 1.3–2.6), based on 43 cases. Men with 'substantial' exposure also had a RR for Hodgkin's lymphoma of 2.0 (90% CI, 1.0–4.1), based on 12 cases. There was no increased risk for cancers of the bladder (1.0; 0.8–1.2; 91 cases) or kidney (1.1; 0.8–1.4; 39 cases) or for non-Hodgkin's lymphoma (0.8; 0.6–1.1; 35 cases). The risks were adjusted for age, socioeconomic status, ethnic group, cigarette smoking and blue–/white–collar job history, and for all potential confounders on which information was available. Of the 739 exposed men, 21% had been employed in the construction trade, mostly as painters.

4. Summary of Data Reported and Evaluation

4.1 Exposures

Petroleum solvents are hydrocarbon mixtures which can be grouped into three broad categories on the basis of their boiling ranges and solvent strengths, as follows: special boiling range solvents, boiling range, 30–160°C; white spirits, 130–220°C; and high-boiling aromatic solvents, 160–300°C. Within these broad solvent categories, individual solvents (typically boiling within narrower ranges of 15–30°C) are composed of aliphatic, alicyclic and aromatic hydrocarbons in varying amounts, depending on refining process and end use. Although the content of benzene in petroleum solvents is now generally less than 1% in nonhydrogenated special boiling range solvents and less than 0.1% in other solvents, higher amounts were commonly present in the past.

Exposure to petroleum solvents is widespread in many occupations, including painting, printing, use of adhesives, rubber processing and degreasing. High exposure levels have been measured in many of these occupational environments.

4.2 Experimental carcinogenicity data

A single study in rats exposed by inhalation to a high-boiling aromatic solvent was of insufficient duration to allow an evaluation of carcinogenicity.

4.3 Human carcinogenicity data

In a single case–control study of cancer at many sites, potential long, high exposure to 'mineral spirits' was associated with increased risks for squamous-cell lung cancer and prostatic cancer. In two case–control studies, one of primary liver cancer and one of Hodgkin's disease, an association with organic solvents, including white spirits, was seen. The results of these studies could not be evaluated with regard to petroleum solvents themselves.

4.4 Other relevant data

In humans, petroleum solvents cause nonallergic contact dermatitis and adverse effects on the central nervous system.

In experimental animals, samples of petroleum solvents with a high aromatic content had greater acute toxicity and were more irritating than those that were virtually aromatic-free. A special boiling range solvent containing *n*-hexane induced chronic toxicity in the peripheral nervous system of experimental animals.

In two studies of malformations in the children of women who had been exposed to petroleum solvents during the first trimester of pregnancy, the numbers of cases were small and the mothers had also been exposed to other substances.

A rubber solvent (special boiling range solvent) induced chromosomal aberrations but not sister chromatid exchange in cultured human cells. Another special boiling range solvent did not induce chromosomal aberrations in cultured mammalian cells, gene conversion in yeast or mutation in bacteria. A sample of white spirits did not induce chromosomal aberrations in mice *in vivo*, sister chromatid exchange in human cells or mutation in bacteria. (See Appendix 1.)

4.5 Evaluation[1]

There is *inadequate evidence* for the carcinogenicity of petroleum solvents in humans.

There is *inadequate evidence* for the carcinogenicity of high-boiling aromatic solvents in experimental animals.

No data were available on the carcinogenicity of special boiling range solvents or white spirits in experimental animals.

Overall evaluation

Petroleum solvents *are not classifiable as to their carcinogenicity to humans (Group 3)*.

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[1] For definitions of the italicized terms, see Preamble, pp. 27-30.

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