EUROPEAN COMMISSION
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Substances covered by Part 1, Annex I, of the Seveso II Directive

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Introduction

Philosophy behind the “Seveso II” Directive

In the “Seveso II” Directive (Council Directive 96/82/EC), generic criteria are as far as possible used as the basis for the inclusion of substances under the Directive, since the current extensive listing of substances has been found inflexible and inappropriate. The assignment of substances into one of the categories in Part 2 of Annex I is based on classification systems addressing the intrinsic properties of substances and established in the Directives 67/548/EEC, 88/379/EEC and 78/631/EEC.

However, for some substances it is desirable to establish higher or lower thresholds than they would have according to their category. The reasons for this may be a combination of technical ones (since the classification system address the intrinsic properties of substances rather than the potential to cause a major accident), industrial or pragmatic (a reasonable number of establishments to be covered). These substances are listed in Part 1 of Annex I.

In the Seveso II Directive, differentiation for storage and process of dangerous substances is no longer made. This change is explained by the fact that the application of the Directive is based upon the potential to create a major accident, which is supposed to be identical for the same quantity of dangerous substance wherever it occurs.

The thresholds are set in order to identify those establishments that should be covered by the Directive. These thresholds do not necessarily correspond to the lowest amount of substance that has the potential to cause a major accident.

Scope of the report

This report aims to describe selected properties of substances listed in Part 1 of Annex I, together with an explanation of their inclusion.

The first part of the report consists of a table listing these substances, their classification according to Directive 67/548/EEC (including 22nd ATP), existing thresholds and new “Seveso II” thresholds.

In the second part, selected properties, use, storage/transport conditions, number of installations covered by the present Seveso Directive (based on information given by the Competent Authorities up to and including 1990) as well as the reason for the inclusion in Part 1 of Annex I of the Seveso II Directive, are described for each substance.

In Annex 1 of this report, risk phrases according to Directive 67/548/EEC are listed.

Part A: Classification and thresholds of substances listed in Part 1 of Annex I

Substance name	**Listing in Annex I to Directive 67/548/EEC (including 22nd ATP)**	**Existing thresholds Directive 82/501/EEC (tonnes)**	**New thresholds Directive 96/82/EC (tonnes)**
Ammonium nitrate	Not listed in Annex I to Dir. 67/548/EEC	350/2500 (Annex II) 2500 (Annex III)	350/2500
Ammonium nitrate fertilisers	Not listed in Annex I to Dir. 67/548/EEC	1250/10000 (Annex II) 5000 (Annex III)	1250/5000
Arsenic pentoxide, arsenic (V) acid and/or salts	Carc.cat.1: R45, T: R23/25	10/200 (Annex II: category criteria) 0.5 (Annex III)	1/2
Arsenic trioxide, arsenious (III) acid and/or salts	Carc.cat 1: R45, T+: R28, C: R34 (As-trioxide) T: R23/25 (acid and salts)	5/20 resp. 10/200 (Annex II: category criteria) 0.1 (Annex III)	/0.1
Bromine	T+: R26, C: R35	50/500 (Annex II) 500 (Annex III)	20/100
Chlorine	T: R23, Xi: R36/37/38, N: R50	10/75 (Annex II) 25 (Annex III)	10/25
Nickel compounds in inhalable powder form (nickel monoxide, nickel dioxide, nickel sulphide, trinickel disulphide, dinickel trioxide)	Carc.cat.1: R49, R43	1 (Annex III)	/1
Ethyleneimine	T+: R26/27/28, F: R11, N: R51-53, Carc.cat.2: R45, Muta.cat.2: R46, C: R34	5/20 (Annex II: category criteria) 50 (Annex III)	10/20
Fluorine	T+: R26, R7, C: R35	5/20 (Annex II: category criteria)	10/20
Formaldehyde (Conc. 🕘 90 %)	T: R23/24/25, Carc.cat.3: R40, C: R34, R43	5/50 (Annex II) 50 (Annex III)	5/50
Hydrogen	F+: R12	5/50 (Annex II) 50 (Annex III)	5/50
Hydrogen chloride (liquefied gas)	T: R23, C: R35	25/250 (Annex II) 250 (Annex III)	25/250
Lead alkyls	T+: R26/27/28, R33, Repr.cat.1: R61, Repr.cat.3: R62 N: R50-53	5/50 (Annex II), 50 (Annex III) (tetraethyl lead or tetramethyl lead)	5/50
Liquefied extremely flammable gases (including LPG) and natural gas	F+: R12	50/200 (Annex II: category criteria) 200 (Annex III)	50/200
Acetylene	F+: R12, R5, R6	5/50 (Annex II) 50 (Annex III)	5/50
Ethylene oxide	F+: R12, T: R23, Carc.cat.2: R45, Muta.cat.2: R46, Xi: R36/37/38	5/50 (Annex II) 50 (Annex III)	5/50
Propylene oxide	F+: R12, Carc.cat.2: R45, Xn:R20/21/22, Xi: R36/37/38	5/50 (Annex II) 50 (Annex III)	5/50

Substance name	**Listing in Annex I to Directive 67/548/EEC (including 22nd ATP)**	**Existing thresholds Directive 82/501/EEC (tonnes)**	**New thresholds Directive 96/82/EC (tonnes)**
Methanol	T: R23/25, F: R11	10/200 (Annex II: category criteria)	500/5000
4,4'-Methylenebis (2-chloroaniline) and/or salts, in powder form	Carc.cat.2: R45, N: R50-53, Xn: R22	0.01 (Annex III)	/0.01
Methylisocyanate	F+: R12, T: R23/24/25, Xi: R36/37/38	0.15/0.15 (Annex II) 0.15 (Annex III)	/0.15
Oxygen	O: R8	200/2000 (Annex II) 2000 (Annex III, liq.)	200/2000
Toluene di-isocyanate	T: R23, Xi: R36/37/38, R42	10/100 (Annex II)	10/100
Carbonyl dichloride (phosgene)	T+: R26, C: R34	0.75/0.75 (Annex II) 0.75 (Annex III)	0.3/0.75
Arsenic trihydride (arsine)	T+: R26, F+: R12, Xn: R48/20, N: R50-53	5/20 (Annex II: category criteria) 0.01 (Annex III)	0.2/1
Phosphorus trihydride (phosphine)	Not listed in Annex I to Dir. 67/548/EEC	5/20 (Annex II: category criteria) 0.1 (Annex III)	0.2/1
Sulphur dichloride	R14, C: R34, Xi: R37	1 (Annex III)	1/1
Sulphur trioxide	Not listed in Annex I to Dir. 67/548/EEC	15/100 (Annex II) 75 (Annex III)	15/75
Polychlorodibenzo-furans and polychlorodibenzo-dioxins (including TCDD), calculated as TCDD equivalents	Not listed in Annex I to Dir. 67/548/EEC	0.001 (Annex III; 2,3,7,8-TCDD) 0.1 (Annex III; 1,2,3,7,8,9-HxCDD)	/0.001 (2,3,7,8-TCDD equivalents)
Automotive petrol and other petroleum spirits	F+: R12	5000/50000 (Annex II: category criteria) 50000 (Annex III)	5000/50000
4-Aminobiphenyl and/or its salts	Carc.cat.1: R45. Xn: R22	0.001 (Annex III)	0.001/0.001
Benzidine and/or salts	Carc.cat.1: R45, Xn: R22, N: R50-53	0.001 (Annex III)	0.001/0.001
Bis(chloromethyl)ether	Carc.cat.1: R45, T+: R26, T: R24, R10, Xn: R22	5/20 (Annex II: category criteria) 0.001 (Annex III)	0.001/0.001
Chloromethyl methyl ether	Carc.cat.1: R45, F: R11, Xn: R20/21/22	5000/50000 (Annex II: category criteria) 0.001 (Annex III)	0.001/0.001
Dimethylcarbamoyl chloride	Carc.cat.2: R45, T: R23, Xn: R22, Xi: R36/37/38	10/200 (Annex II: category criteria) 0.001 (Annex III)	0.001/0.001
Dimethylnitrosamine	Carc.cat.2: R45, T+: R26, T: R25-48/25, N: R51-53	5/20 (Annex II: category criteria) 0.001 (Annex III)	0.001/0.001
Hexamethylphosphoric triamide	Carc.cat.2: R45, Muta.cat.2: R46	0.001 (Annex III)	0.001/0.001
2-Naphtylamine and/or salts	Carc.cat.1: R45, Xn: R22, N: R51-53	0.001 (Annex III)	0.001/0.001
1,3-Propanesultone	Carc.cat.2: R45, Xn: R21/22	0.001 (Annex III)	0.001/0.001
4-Nitrodiphenyl	Carc.cat.2: R45		0.001/0.001

Part B: Properties, use, storage conditions and explanation of the inclusion of substances listed in Part 1 of Annex I

Ammonium nitrate

Properties
Oxidising, colourless crystals, m.p. 170°C. It decomposes at 210°C, with evolution of toxic fumes of nitrogen oxides. In the absence of impurities it is difficult, but not impossible, to cause ammonium nitrate to detonate; it may explode under confinement and high temperatures. Ammonium nitrate forms heat or shock sensitive explosive mixtures with a wide range of substances (e.g. organic fuel, powdered metals, acetic acid, sugar). Can react vigorously with reducing materials. It ignites on contact with a number of substances, for instance sodium chloride.
Not listed in Directive 67/548/EEC, Annex I.

Use
Production of fertilisers and explosives.

Storage/transport conditions
Contained in bags and tanks. 28 sites (including the fertiliser form below) are covered by Annex III of the Seveso directive (threshold 2500t and 5000t respectively).

Reason for inclusion in Part 1 of Annex I
Pure ammonium nitrate would probably be classified as “oxidising” according to Directive 67/548/EEC. Based on generic criteria in Part 2, thresholds would be 50/200 tonnes. Ammonium nitrate contaminated with combustible substances (above ~0.2%) would probably be classified as “explosive” with thresholds 50/200 tonnes.
However, ammonium nitrate is at present covered by Annex II at 350/2500 tonnes and by Annex III at 2500 tonnes. These thresholds were carried over to the new directive.
Ammonium nitrate or ammonium nitrate fertilisers have been involved in 2% of the accidents reported in MARS up to and including 1993.

Ammonium nitrate fertilisers

Properties
Oxidising. The fertiliser grade of ammonium nitrate is said not to be explosive. Not listed in Directive 67/548/EEC, Annex I.

Use
Fertiliser.

Storage/transport conditions
Contained in bags or tanks. 28 sites (including the ammonium nitrate form above) are covered by Annex III of the Seveso directive (threshold 5000t and 2500t respectively).

Reason for inclusion in Part 1 of Annex I
Ammonium nitrate fertilisers according to note 2 to Part 1, would probably be

classified as “oxidising” based on criteria in Directive 67/548/EEC. Based on generic criteria in Part 2, thresholds would be 50/200 tonnes.

At present ammonium nitrate fertilisers are covered by Annex II at 1250/10000 tonnes and by Annex III at 5000 tonnes. The original Commission proposal to include ammonium nitrate fertilisers at thresholds 1250/5000 tonnes was agreed on. Ammonium nitrate or ammonium nitrate fertilisers have been involved in 2% of the accidents reported in MARS up to and including 1993.

Arsenic pentoxide

Properties

Very toxic, white amorphous lumps or powder (m.p. 315°C, decomposition upon heating). Odourless. Fire may produce irritating or poisonous gases. It reacts with metal, emitting toxic arsine gas.

The presumable oral lethal dose is 5-50 mg/kg. It irritates eyes, nose, throat and stomach. Symptoms usually appear 1/2-1 hour after ingestion, but may also be delayed. Chronic exposure may cause nerve damage, may change cellular composition of the blood and may induce structural changes in blood components. Carcinogenic to humans.

LD50 orl rat: 8 mg/kg. IDLH: 80 mg/m^3.

Listed in Directive 67/548/EEC, Annex I, as “carcinogen cat. 1, may cause cancer (R45) and toxic by inhalation and if swallowed (R23/25)”. Reclassification of toxicity (animal tests indicate “very toxic”) is not to be considered by the Annex I (Directive 67/548) working group in the near future.

Use

It is used as an ingredient in wood preservatives, as a herbicide, as an insecticide, in glass and as a chemical intermediate.

Storage/transport conditions

Contained in drums etc.

124 sites are covered by Annex III of the Seveso Directive with respect to Arsenic (V) compounds (threshold 0.5 tonnes).

Reason for inclusion in Part 1 of Annex I

Based on generic criteria, thresholds would be 50/200 tonnes (“toxic”).

It is carcinogenic, but not considered as potent as to be listed under “Carcinogens”. However, member states have concern for this substance.

The thresholds have been raised (to 1/2 t) because it was argued that too many establishments would be covered with the existing Annex III threshold (0.5 t).

Arsenic (V) acid and its salts

Properties

Very toxic, white to colourless solids (arsenic acid and its sodium salt; m.p. 35.5°C (hemihydrate), calcium salt m.p. 1455°C) with no odour. (Other salts also exist). When heated they decompose and emit toxic fumes of arsenic.

The presumable oral lethal dose is 5-50 mg/kg. It irritates eyes, nose, throat and stomach. Symptoms usually appear 1/2-1 hour after ingestion, but may also be delayed. Chronic exposure may cause nerve damage, may change cellular composition of the blood and may induce structural changes in blood components. Carcinogenic to humans.

Arsenic acid: LD50 orl rat: 48 mg/kg.

Arsenic acid, calcium salt: LD50 orl rat: 20 mg/kg. IDLH: 100 mg/m^3.

Arsenic (V) acid and its salts are listed in Directive 67/548/EEC, Annex I, as "carcinogen cat. 1, may cause cancer (R45) and toxic by inhalation and if swallowed (R23/25)".

Use

Arsenic acid: It is used as an ingredient in wood preservatives, as a herbicide, as desiccant for cotton, in glass and as a chemical intermediate

Arsenic acid, calcium salt: predominantly used as an insecticide and herbicide.

Arsenic acid, sodium salt: predominantly used as insecticide.

Storage/transport conditions

Contained in drums etc.

124 sites are covered by Annex III of the Seveso Directive with respect to Arsenic (V) compounds (threshold 0.5 tonnes).

Reason for inclusion in Part 1 of Annex I

Based on generic criteria, thresholds would be 50/200 tonnes ("toxic").

It is carcinogenic, but not considered so potent as to be listed under "Carcinogens". However, member states have concern about this substance.

The thresholds have been raised (to 1/2 t) because it was argued that too many establishments would be covered with the existing Annex III threshold (0.5 t).

Arsenic trioxide

Properties

Very toxic, white or transparent, glassy amorphous lumps or crystalline powder (sublimes at 193°C) without any odour. Toxic fumes of arsenic trioxide and arsine may be formed in fire situations. The presumable oral lethal dose is 5-50 mg/kg. It causes acute gastrointestinal and central nervous system symptoms. Renal and hepatic damage may also occur. Symptoms of acute poisoning may appear after 1/2 hour to several hours. Carcinogenic to humans upon chronic exposure (lung and lymphatic cancers).

LD50 orl rat: 4.5 mg/kg. IDLH: 14 mg/m^3.

Listed in Directive 67/548/EEC, Annex I, as "carcinogen cat. 1, may cause cancer (R45), very toxic if swallowed (R28) and causes burns (R34)".

Use

It is used as a wood preservative, as an intermediate for insecticides, herbicides and fungicides, as a rodenticide, in pharmaceuticals, in the purification of syntethic gas and as a decolouring and refining agent in glass manufacture and as a chemical intermediate.

Storage/transport conditions

Contained in drums etc.

51 sites are covered by Annex III of the Seveso directive with respect to Arsenic (III) compounds (threshold 0.1 tonnes).

Reason for inclusion in Part 1 of Annex I

Based on generic criteria, thresholds would be 5/20 tonnes (“very toxic”).

It is carcinogenic, but not considered so potent as to be listed under “Carcinogens”. However, member states have concern about this substance.

Included at existing Annex III threshold (0.1 t).

Arsenious (III) acid and its salts

Properties

Arsenious acid is a very toxic, colourless solution of arsenic oxide in water. The monosodium salt is a very toxic white or greyish powder and the potassium salt is a very toxic white hygroscopic powder. (Other salts also exist).

Fire may produce irritating and toxic fumes.

Arsenious acid: LD50 orl rat: 14.6 mg/kg. Carcinogenic to humans.

Arsenious acid, sodium salt: LDLo orl rabbit: 7.5 mg/kg. Carcinogenic to humans.

Arsenious acid, potassium salt: LDLo orl dog: 3 mg/kg. Carcinogenic to humans.

Not separately listed in Directive 67/548/EEC, Annex I, but is included under “arsenic compounds with the exception of arsenic trioxide, arsenic pentoxide, and arsenic acid and its salts” as “toxic by inhalation and if swallowed (R23/25)”.

Use

Arsenious acid, potassium salt may be used as a reducing agent. However, it is unclear whether it is currently used at all.

Arsenious acid, monosodium salt is used in treating wine against certain scale diseases, in wood preservation, as a reagent in the preparation of methylene iodide, as a corrosion inhibitor, as a herbicide and pesticide and in manufacturing of arsenical soap for use on skin.

Storage/transport conditions

Contained in drums etc.

51 sites are covered by Annex III of the Seveso directive with respect to Arsenic (III) compounds (threshold 0.1 tonnes).

Reason for inclusion in Part 1 of Annex I

Based on generic criteria, thresholds would be 50/200 tonnes ("toxic").
It is supposed to be carcinogenic (although not classified as such). However, member states have concern about this substance.
Included at existing Annex III threshold (0.1 t).

Bromine

Properties

Very toxic, non-flammable, corrosive, oxidising, heavy, dark reddish-brown liquid (b.p. 59.5°C, m.p. -7.25°C) with suffocating odour. Vapour density: 5.54 at 20°C.
Explosive reactions may occur with a wide variety of substances (e.g. acetylene, ammonia, phosphorous). It may cause ignition of organic material.
Vapours cause acute as well as chronic poisoning. It has cumulative properties. Irritates eyes and respiratory tract. Ingestion may cause death due to circulatory collapse and asphyxiation from swelling of the respiratory tract.
LDLo orl hmn: 14 mg/kg. LCLo inh hmn: 1000 ppm. IDLH: 10 ppm (66 mg/m^3).
Listed in Directive 67/548/EEC, Annex I, as "very toxic by inhalation (R26) and causes severe burns (R35)".

Use

It is used in the manufacture of medicinal bromine compounds, as a fire-retardant for plastics, in photography, in shrink-proofing wool, in organic synthesis, as a solvent, as intermediate for fumigants, as a fire-extinguishing liquid, as an analytical chemical, as a refrigerant, dehumidifying reagent, as well as for swimming pool sanitation and water purification. It is also used for gold extraction, military gas, bleaching fibres and silks and in the manufacture of anti-knock compounds.

Storage/transport conditions

6 producers in Europe and import from Israel via Rotterdam. Sold in tanks containing about 15 tonnes, or in containers of maximum 450 litres.
25 sites are covered by Annex III of the Seveso directive (threshold 500 tonnes).

Reason for inclusion in Part 1 of Annex I

Based on generic criteria, thresholds would be 5/20 tonnes ("very toxic").
Included at lower thresholds (20/100) than existing Annex II and III thresholds (following discussions in Expert working group) to bring it more into line with thresholds for chlorine. Although bromine is classified as "very toxic" whereas chlorine is "toxic", its major accident potential is considered to be lower.
Bromine has been involved in 1% of the accidents reported in MARS up to and including 1993.

Chlorine

Properties

Toxic, non-flammable, irritating, reactive, oxidising, greenish-yellow gas (b.p.-34.5°C) with suffocating odour.

Vapour density: 2.46 at 20°C.

May ignite other combustible materials (wood, paper, oil etc.). Mixture with fuels may cause explosion. Most combustible materials will burn in chlorine as they do in oxygen. Combines with water or steam to produce toxic and corrosive fumes of hydrochloric acid.

Chlorine is toxic by inhalation. Very irritating by inhalation (if the lung tissues are attacked, pulmonary oedema may result). Contact may cause burns to skin and eyes. A concentration of 3.5 ppm produces a detectable odour, 15 ppm causes immediate irritation of the throat. Concentrations of 50 ppm are dangerous for even short exposures and 1000 ppm may be fatal even when the exposure is brief.

LC50 inh rat: 293 ppm/1hr (0.86 mg/l/1hr). LCLo inh man: 2.53 mg/l/30 min. IDLH: 25 ppm (74 mg/m^3).

Listed in Directive 67/548/EEC, Annex I, as “toxic by inhalation (R23), irritating to eyes, respiratory system and skin (R36/37/38) and very toxic to aquatic organisms (R50)”.

Use

Chlorine is used in the manufacture of synthetic rubber and plastics (polyvinyl chloride, neoprene), chlorinated hydrocarbons, hydrogen chloride, metallic chlorides. Also used for water purification, in processing of food and in shrinkproofing wool.

Storage/transport conditions

Stored/transported as liquefied gas under pressure.

240 sites are covered by Annex III of the Seveso directive (threshold 25 tonnes).

Reason for inclusion in Part 1 of Annex I

Based on generic criteria, thresholds would be 50/200 tonnes (“toxic”). However, chlorine has been included with the lower Annex II threshold (10 t) and the Annex III threshold (25 t). It is widely used and history has shown that it has a high major accident potential.

Chlorine has been involved in 11% of the accidents reported in MARS up to and including 1993.

Nickel oxides and sulphides in inhalable powder form

Properties

Human carcinogens. When nickel sulphides are heated to decomposition, they emit toxic fumes of sulphur oxides.

Listed in Directive 67/548/EEC, Annex I, as “carcinogen cat. 1, may cause cancer by inhalation (R49) and may cause sensitisation by skin contact (R43).”

Use

Nickel sulphides are used for manufacture of catalysts.
Dinickel trioxide is used in storage batteries.
Nickel monoxide is used in fuel cell electrodes and for manufacture of nickel salts.

Storage/transport conditions

Sold in drums etc.
81 sites are covered by Annex III of the Seveso directive (threshold 1 tonne) with respect to nickel compounds (including metal and carbonates).

Reason for inclusion in Part 1 of Annex I

Based on generic criteria, these substances would not be covered by the Directive.
They are carcinogenic, but not considered so potent as to be listed under "Carcinogens". However, member states have concern about this substance.
Included at existing Annex III threshold (1 t).

Ethyleneimine

Properties

Very toxic, flammable, colourless liquid (b.p. 56°C) with strong ammoniacal odour. Flash point: -11°C. Vapour density: 1.5.
Hazardous polymerisation may occur (e.g. in fires, contact with acids).
Very toxic with a presumable oral lethal dose of 5-50 mg/kg which is approximately 7 drops to 1 teaspoonful for a 70 kg person. It causes severe blistering with third degree chemical burns of the skin. Severe exposure may lead to overwhelming pulmonary oedema. Hemorrhagic congestion of all internal organs may occur.
LD50 orl rat: 15 mg/kg, LC50 inh rat: 100 mg/m^3/2 hrs. IDLH: 22 ppm (40 mg/m3). Probable human carcinogen.
Listed in Directive 67/548/EEC, Annex I, as "very toxic by inhalation, in contact with skin and if swallowed (R26/27/28), highly flammable (R11), carcinogen cat. 2, may cause cancer (R45), mutagen cat. 2, may cause heritable genetic damage (R46), causes burns (R34), toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment (R51-53)."

Use

Products of polymerisation of ethyleneimine are used in the paper industry and as flocculation aids. Ethyleneimine is also used in textile chemicals, adhesives, binders, petroleum refining chemicals, fuels and lubricants, coating resins, varnishes, lacquers, agricultural chemicals, cosmetics, ion exchange resins, photographic chemicals and surfactants.

Storage/transport conditions

3 sites are covered by Annex III of the Seveso directive (threshold 50 tonnes).

Reason for inclusion in Part 1 of Annex I

Based on generic criteria, thresholds would be 5/20 tonnes (“very toxic”). The original commission proposal and existing Annex III thresholds was however 50t.

Member states saw no reason to keep the 50 t threshold, and proposed the thresholds to be in accordance with the generic criteria. For pragmatic reasons, the lower threshold was raised to 10 tonnes. Thus included at thresholds 10/20 tonnes.

Fluorine

Properties

Very toxic, corrosive, oxidising, reactive, pale yellow gas (b.p. -188°C) with pungent odour. Gas density: 1.7. Reacts vigorously with most oxidisable substances at room temperature, frequently with ignition.

LC50 inh rat: 185 ppm/1hr. IDLH: 25 ppm (39 mg/m^3).

Listed in Directive 67/548/EEC, Annex I, as “may cause fire (R7), very toxic by inhalation (R26) and causes severe burns (R35)”.

Use

Fluorine is used for the production of fluorides and fluorocarbons, as one component in liquid rocket fuel, in chemical lasers.

Storage/transport conditions

Very few producers. Transport in tanks prohibited according to the ADR/RID agreement. Not listed in the Seveso Directive.

Reason for inclusion in Part 1 of Annex I

Based on generic criteria, thresholds would be 5/20 tonnes (“very toxic”). The original commission proposal was however to include fluorine (which is not listed in Annex III of the existing directive) at the same thresholds as for chlorine (10/25 t). This proposal followed after discussions in an expert group.

Member states proposed the higher threshold to be in accordance with generic criteria. But, for pragmatic reasons, the lower threshold was proposed to be raised to 10 tonnes. Thus included at thresholds 10/20 tonnes.

Formaldehyde (concentration ≥ 90 %)

Properties

Toxic, corrosive gas (b.p. -19°C, vapour density 1.08) with strong, pungent odour. It is a readily polymerisable gas. It is soluble in water (52%) and alcohol.

IDLH: 100 ppm (124 mg/m^3).

Listed in Directive 67/548/EEC, Annex I, as “toxic by inhalation, in contact with skin, if swallowed (R23/24/25), corrosive, causes burns (R34), carcinogen, cat.3, possible risk of irreverible effects (R40) and may cause sensitisation by skin contact (R43)”.

Use

Urea and melamine resins, polyacetal and phenolic resins, ethylene glycol, fertiliser, dyes, medicine (disinfectant, germicide), industrial sterilant, preservative, corrosion inhibitor in oil wells, durable-press treatment of textile fabrics.

Storage/transport conditions

Contained in drums and tanks. No sites covered by Annex III of the Seveso directive (threshold 50 tonnes).

Reason for inclusion in Part 1 of Annex I

Based on generic criteria, thresholds would be 50/200 tonnes (“toxic”).
Included at existing thresholds, 5/50 tonnes.

Hydrogen

Properties

Colourless, odourless, extremely flammable gas (b.p. -252°C). Vapour density 0.069. Classed as an asphyxiant gas (can cause unconsciousness and death by replacing air). Severe explosion hazard when exposed to heat, flame or oxidisers. Flammable or explosive when mixed with e.g. air, oxygen, chlorine, fluorine.
Listed in Directive 67/548/EEC, Annex I as “extremely flammable (R12)”.

Use

Production of ammonia and methanol, hydrocracking, hydroforming and hydrofining of petroleum, hydrogenation of vegetable oils, hydrogenolysis of coal, reducing agent for organic synthesis and metallic ores, as oxyhydrogen flame for high temperatures, making hydrochloric and hydrobromic acids. In liquid form hydrogen is used as coolant and missile fuel.

Storage/transport conditions

Stored in steel cylinders and tanks. 7 sites covered by Annex III of the Seveso directive (threshold 50 tonnes).

Reason for inclusion in Part 1 of Annex I

Based on generic criteria, thresholds would be 10/50 tonnes (“extremely flammable”).
Included at existing thresholds, 5/50 tonnes.
Hydrogen has been involved in 7% of the accidents reported in MARS up to and including 1993.

Hydrogen chloride (liquefied gas)

Properties

Colourless, strongly corrosive, non-flammable gas with suffocating odour (b.p. -85°C). Vapour density 1.268.

Strong corrosive irritant to the skin, eyes and mucous membranes. Explosive reactions with e.g. sodium and ignition on contact with e.g. fluorine or carbides. When heated to decomposition it emits toxic chloride fumes. IDLH: 100 ppm (154 mg/m^3).

Listed in Directive 67/548/EEC, Annex I as "toxic by inhalation (R23) and causes severe burns (R35)".

Use

Production of vinyl chloride and alkyl chlorides. Also used in hydrochlorination, polymerisation, alkylation, isomerisation and nitration reactions.

Storage/transport conditions

Cylinders and tanks are used for storage/transport. 2 sites covered by Annex III of the Seveso directive (threshold 250 tonnes).

Reason for inclusion in Part 1 of Annex I

Based on generic criteria, hydrogen chloride would not be covered by the Directive. However, several accidents involving hydrogen chloride have occurred (7% of the accidents reported in MARS up to and including 1993).

Included at existing thresholds 25/250 t.

Lead alkyls

Properties

Triethyl lead, tetraethyl lead (b.p. 198-202°C) and tetramethyl lead (b.p. 110°C) are liquids. Lead alkyls are rapidly absorbed by the respiratory and gastrointestinal systems and through the skin. They are particularly toxic to the central nervous system. Lead is a cumulative poison (increasing amounts build up in the body and eventually reach a point where symptoms occur). Lead alkyls are experimental teratogens and have effects on reproduction. Tetraethyl lead is converted in the body to triethyl lead which is a more severe neurotoxin than inorganic lead.

When heated to decomposition they emit toxic lead fumes.

Listed in Directive 67/548/EEC, Annex I as "very toxic by inhalation, in contact with skin or if swallowed (R26/27/28), danger of cumulative effects (R33), may cause harm to the unborn child (R61), possible risk of impaired fertility (R62), very toxic to aquatic organisms and may cause long term adverse effects in the aquatic environment (R50-53)".

Use

Tetraethyl lead and tetramethyl lead are used as octane enhancers for petrols, tetraethyl lead also in ethylation operations.

Storage/transport conditions

Stored/transported in drums and tanks. 38 sites (tetraethyl lead) and 15 sites (tetramethyl lead) are covered by Annex III of the Seveso directive (thresholds 50 tonnes).

Reason for inclusion in Part 1 of Annex I

Based on generic criteria, thresholds would be 5/20 tonnes (“extremely toxic”).
However, included at existing thresholds, 5/50 tonnes.

Liquefied extremely flammable gases (including LPG) and natural gas

Properties

Extremely flammable (R12). Risk of fire and explosion.
LPG: colourless flammable, noncorrosive, nontoxic gas obtained as a by-product in petroleum refining or natural petroleum manufacture, e.g. butane, propane, propene and their mixtures.
Natural gas: colourless flammable, asphyxiant gas composed of 85% methane, 10% ethane, the balance being made up of propane, butane and nitrogen.

Use

LPG: domestic, industrial and automotive fuel, in welding, brazing and metal cutting, and as an intermediate.
Natural gas: fuel and cooking gas, in ammonia synthesis, petrochemical feedstocks, carbon black manufacture.

Storage/transport conditions

LPG: very large stockages in underground cavities and in tanks. Wholesalers’ stock (cylinders) can be in the order of 50 tonnes.
Natural gas: Very large stockages in tanks. Sold via tankers and pipelines.

Reason for inclusion in Part 1 of Annex I

Based on generic criteria, thresholds would be 10/50 tonnes (“extremely flammable”).
The original Commission proposal was to list “LPG (including propane and butane)” and “Natural gas or other combustible gases” in Part 1 (thresholds 50/200 tonnes in order not to include too many sites). This would however lead to unfair competition for sites using other liquefied gases. Thus, the two entries were changed and combined to read “liquefied extremely flammable gases (including LPG) and natural gas” (50/200 tonnes).
LPG and other C2, C3 and C4 hydrocarbons have been involved in 16% of the accidents reported in MARS up to and including 1993, whereas natural gas and methane have been involved in 5% of the MARS accidents.

Acetylene

Properties

Flammable, reactive, unstable, colourless gas (sublimes at -84°C) with ethereal odour. Vapour density: 0.91. Heating may cause explosion, also explosive with or without contact with air. Reacts with heavy metals to form explosive acetylides.
An asphyxiant gas.
Listed in Directive 67/548/EEC, Annex I, as "extremely flammable (R12), heating may cause explosion (R5) and explosive with or without contact with air (R6)".

Use

Acetylene is used in manufacture of vinyl chloride, vinylidene chloride, vinyl acetate, acrylonitrile, acrylates, per- and trichloroethylene, 1,4-butanediol, carbon black and in welding and cutting metals.

Storage/transport conditions

Sold in cylinders, dissolved under pressure in acetone absorbed by a porous mass. Transport in tanks prohibited according to the ADR/RID agreement.
No site is covered by Annex III of the Seveso directive (threshold 50 tonnes).

Reason for inclusion in Part 1 of Annex I

Based on generic criteria, thresholds would be 10/50 tonnes ("extremely flammable"). Acetylene was not listed in the original Commission proposal, but for political reasons it was preferred to specifically name this substance with the existing Seveso Annex II and III thresholds. Thus included at thresholds 5/50 tonnes. Acetylene has been involved in 1% of the accidents reported in MARS up to and including 1993.

Ethylene oxide

Properties

Flammable, toxic, highly reactive, chemically instable, colourless gas (b.p. 10.7°C) with ethereal odour. Vapour density: 1.52. Severe explosion hazard when exposed to heat or flame. Vapour forms explosive mixtures with air over a wide range. Irritating vapours are generated when heated. Decomposition products are explosive.
Neurological disorders and even death after exposure have been reported. Probable human carcinogen.
LC50 inh rat: 1462 ppm/4 hrs. LD50 orl rat: 72 mg/kg. IDLH: 800 ppm (1460 mg/m^3).
Listed in Directive 67/548/EEC, Annex I, as "extremely flammable (R12), toxic by inhalation (R23), carcinogen cat. 2, may cause cancer (R45), mutagen cat.2, may cause heritable genetic damage (R46) and irritating to eyes, respiratory system and skin (R36/37/38)".

Use

Ethylene oxide is a chemical intermediate for ethylene glycol (50% of the world production of ethylene oxide is used for production of ethylene glycol which then is used for the manufacture of polyester and as antifreezing agent), nonionic surfactants, glycol ethers, ethanolamines, triethylene glycol and polyethylene glycol. Used as a fumigant for foodstuffs and textiles, for sterilising instruments and as an agricultural fungicide.

Storage/transport conditions

Stored in steel tanks, small cisterns or cylinders (liquefied gas under pressure, under inert gas). Some industries are fed via pipe-lines.
26 sites are covered by Annex III of the Seveso directive (threshold 50 tonnes).

Reason for inclusion in Part 1 of Annex I

Based on generic criteria, thresholds would be 10/50 tonnes (“extremely flammable”). Ethylene oxide was not listed in the original Commission proposal, but for political reasons it was preferred to specifically name this substance with the existing Seveso Annex II and III thresholds. Thus included at thresholds 5/50 tonnes.
Ethylene oxide has been involved in 3% of the accidents reported in MARS up to and including 1993.

Propylene oxide

Properties

Extremely flammable, colourless liquid (b.p. 34.2°C) with sweet, alcoholic odour like natural gas, ether or benzene. Flash point: -37°C. Vapour density: 2.0.
Vapours form explosive mixture with air. Explosion hazard is severe when exposed to flame. Hazardous polymerisation may occur (e.g. high temperatures, alkalis, anhydrous chlorides of iron, tin and aluminium).
Exposure may entail mild depression of the central nervous system and eye, nasal and lung irritation. Probable human carcinogen.
LD50 orl rat: 930 mg/kg. LCLo inh rat: 4000 ppm/4 hrs. IDLH: 200 ppm (480 mg/m^3).
Listed in Directive 67/548/EEC, Annex I, as “extremely flammable (R12), carcinogen cat. 2, may cause cancer (R45), harmful by inhalation, in contact with skin or if swallowed (R20/21/22) and irritating to eyes, respiratory system and skin (R36/37/38)”.

Use

Propylene oxide is essentially used as a chemical intermediate for polyurethane polyols, propylene glycol and dipropylene glycol. It is also used for sterilisation of packaged foods, as a herbicide, in the preparation of lubricants, surfactants and oil demulsifiers.

Storage/transport conditions

Stored in tanks or small cisterns. 23 sites are covered by Annex III of the Seveso directive (threshold 50 tonnes).

Reason for inclusion in Part 1 of Annex I

Based on generic criteria, thresholds would be 10/50 tonnes ("extremely flammable"). Propylene oxide was not listed in the original Commission proposal, but for political reasons it was preferred to specifically name this substance with the existing Seveso Annex II and III thresholds. Thus included at thresholds 5/50 tonnes.

Methanol

Properties

Highly flammable, toxic, clear, colourless liquid (b.p. 64.5°C) with alcoholic odour. Flash point 12.2°C. Vapour density: 1.11. Dangerous fire hazard when exposed to heat, flame or oxidisers. Explosive in the form of vapour when exposed to heat or flame.

A human poison by ingestion. Its main toxic effect is exerted upon the nervous system, particularly the optic nerves and possibly the retinas which can progress to permanent blindness. Once absorbed, methanol is only very slowly eliminated, and it should be regarded as a cumulative poison. In the body, the products formed by its oxidation are formaldehyde and formic acid, which are toxic.

LD50 orl rat: 5628 mg/kg. LC50 inh rat: 64000 ppm/4 hrs (85.1 mg/l/4 hrs). LD50 skn rabbit: 15800 mg/kg. IDLH: 25000 ppm (33200 mg/m^3).

Listed in Directive 67/548/EEC, Annex I, as "highly flammable (R11), toxic by inhalation and if swallowed (R23/25)". (Reclassification of toxicity is not to be considered by the Annex I (Dir. 67/548) working group in the near future).

Use

Methanol is used as a solvent (for nitrocellulose, ethylcellulose, shellac, dyes, etc.), in chemical synthesis (formaldehyde (~40% of world production of methanol is used for the synthesis of formaldehyde), methyl amines, methyl chloride, methyl methacrylate, etc.), fuel (~14% of world production) (mainly for the production of methyl-tert-butylether), and as an antifreeze agent.

Storage/transport conditions

Stored in tanks and in drums. Seems to be a large number of users with stocks of several hundred tonnes. Not listed in the Seveso directive.

Reason for inclusion in Part 1 of Annex I

Based on generic criteria, thresholds would be 50/200 tonnes ("toxic"). Methanol was not listed in the original Commission proposal. Concerns were expressed that a too large number of installations would be covered according to the generic criteria. When methanol is described in chemical reference literature, it is referred to as toxic for humans by ingestion but only mildly toxic by inhalation (in Directive 67/548/EEC classified as toxic if swallowed and toxic by inhalation, though). Since inhalation of gas/vapour and not ingestion is the main intake route in case of a major accident, it was suggested that methanol should be assigned thresholds according to its flammable rather than toxic properties. That would lead to considerably higher thresholds (5000/50000 t). A compromise solution was agreed upon, and methanol was included at thresholds 500/5000 tonnes.

Methanol has been involved in 3% of the accidents reported in MARS up to 1993.

4,4’-Methylenebis(2-chloroaniline), MOCA, and/or salts, in powder form

Properties

MOCA: Tan-coloured pellets (melting range 99-107°C). When heated to decomposition, it emits toxic fumes of chloride and nitrogen oxides. Probable human carcinogen and teratogen..
LD50 orl rat: 2100 mg/kg.
Listed in Directive 67/548/EEC, Annex I, as “carcinogen cat.2, may cause cancer (R45), harmful if swallowed (R22) and very toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment (R50-53).

Use

It is used as curing agent for polyurethanes and epoxy resins.

Storage/transport conditions

Stored in drums etc. 4 sites are covered by Annex III of the Seveso directive (threshold 0.01 tonnes).

Reason for inclusion in Part 1 of Annex I

Based on generic criteria, thresholds would be 200/500 tonnes (“very toxic to aquatic organisms”).
It is carcinogenic, but not considered so potent as to be listed under “Carcinogens”. However, member states have concern about this substance. Since this substance is not considered to be hazardous in form of pellets, it is included only in the form of powder at existing Annex III threshold (0.01 t).

Methyl isocyanate

Properties

Highly flammable, toxic, colourless liquid (b.p. 39.1°C) with sharp odour. Flash point < -7°C. Vapour density 2.0. May be ignited by heat, sparks or flames. Reacts violently with e.g. water (polymerisation, exothermic reactions). Container may explode violently in heat of fire. When heated to decomposition, hydrogen cyanide, nitrogen oxides and carbon oxides may be produced.
Methyl isocyanate attacks the respiratory system, eyes and skin. It can injure the lungs and bronchial airways, cause permanent eye damage and death.
LD50 orl rat: 71 mg/kg. LC50 inh rat: 5 ppm/4 hrs. (0.012 mg/l/4 hrs) IDLH: 20 ppm (47 mg/m^3).
Listed in Directive 67/548/EEC, Annex I, as “extremely flammable (R12), toxic by inhalation, contact with skin and if swallowed (R23/24/25) and irritating to eyes, respiratory system and skin (R36/37/38)”. (Reclassification of toxicity is not to be considered by the Annex I (Directive 67/548) working group in the near future).

Use

Methyl isocyanate is used as an intermediate in the manufacturing of N-methylcarbonate ester and N-methylurea insecticides and herbicides.

Storage/transport conditions

6 sites are covered by Annex III of the Seveso directive (threshold 0.15 tonnes).

Reason for inclusion in Part 1 of Annex I

Based on generic criteria thresholds would be 10/50 tonnes (“extremely flammable”). In view of the Bhopal accident the threshold is maintained at existing Annex II and III level (0.15 t).

Oxygen

Properties

Colourless, odourless, tasteless nonflammable gas (b.p. -218°C). Systemic effects by inhalation: cough, convulsions and other pulmonary changes. In liquid form it can cause severe tissue damage on contact with skin due to extreme cold. An oxidant. A slight increase in the oxygen content in air increases the oxidation or burning rate of many materials. Liquid oxygen can explode on contact with readily oxidisable materials, especially at high temperatures. Under the proper conditions of temperature, pressure, and reagent concentration it can react violently with a number of substances, e.g. acetylene, ammonia, chlorinated hydrocarbons, ethers, hydrogen, hydrocarbons (e.g. petrol, ethylene), metals, organic matter.

Liquid oxygen listed in Directive 67/548/EEC, Annex I, as “oxidising, contact with combustible material may cause fire (R8)”.

Use

Blast furnaces, copper smelting, steel production, manufacture of synthesis gas for production of ammonia, methyl alcohol, acetylene etc., oxidiser for liquid rocket propellants, coal gasification, to replace air in oxidation of municipal and industrial organic wastes, resuscitation, heart stimulant.

Storage/transport conditions

Stored/transported in tanks and cylinders. 15 sites using liquid oxygen are covered by Annex III of the Seveso directive (threshold 2000 tonnes).

Reason for inclusion in Part 1 of Annex I

Based on generic criteria thresholds would be 50/200 tonnes (“oxidising”). Included at existing thresholds, 200/2000 tonnes.

Toluene diisocyanate (TDI)

Properties

Toxic, clear, faintly pale yellow liquid (m.p. 19.5-21.5°C, b.p. 251°C) with sharp, pungent odour. Flash point: 132°C. Vapour density: 6.0. Reacts with compounds containing active hydrogen (may be violent). Reaction with water releases carbon dioxide. Combustible. Explosive in the form of vapour when exposed to heat or flame. When heated to decomposition it emits toxic fumes of nitrogen oxides.

Human systemic effects by inhalation: changes to the eyes and sense of smell, respiratory obstruction, pulmonary and gastrointestinal changes. A severe skin and eye irritant. May be a human carcinogen.

LC50 inh rat: 14 ppm/4 hrs. (0.10 mg/l/4 hrs). IDLH: 10 ppm (72 mg/m^3).

Listed in Directive 67/548/EEC, Annex I, as "toxic by inhalation (R23), irritating to eyes, to respiratory system and to skin (R36/37/38) and may cause sensitisation by inhalation (R42). (Reclassification will be under consideration by the Annex I (Dir 67/548) working group in the "near" future.)

Use

It is used for manufacture of polyurethane foams, elastomers and coatings. Cross-linking agent for nylon 6.

Storage/transport conditions

Sold in rail tanks. Not listed in Annex III of the Seveso directive.

Reason for inclusion in Part 1 of Annex I

Based on generic criteria thresholds would be 50/200 tonnes ("toxic"). This substance was not included in the original Commission proposal. However, it was felt to be politically impossible to raise the threshold in accordance with the generic criteria (TDI is currently listed in Annex II with thresholds 10/100 tonnes). Thus included at existing Annex II level.

Phosgene

Properties

Very toxic, non-flammable, colourless gas (b.p. 8.3°C) with suffocating odour reminiscent of mouldy hay or similar to decaying fruit at room temperature. Vapour density: 3.43 (20°C).

When heated to decomposition or on contact with water or steam, it will react to produce toxic and corrosive fumes.

Phosgene is a long toxicant that causes damage to the capillaries, bronchioles and alveoli of the lungs by decomposition to hydrochloric acid and carbon monoxide. There is little immediate irritant effects upon the respiratory tract, and the warning properties of the gas are therefore very slight. The full effect is not usually apparent until 3 or 4 hours after exposure.

LC50 inh rat: 1400 mg/m^3/30 min. LC50 inh human: 3200 mg/m^3. TCLo inh human: 25 ppm/30 min. IDLH: 2 ppm (8 mg/m^3).

Listed in Directive 67/548/EEC, Annex I, as "very toxic by inhalation" (R26) and causes burns (R34)".

Use
Chemical intermediate for toluene diisocyanate, methyl isocyanate, diphenylmethane-4,4'-diisocyanate, chloroformate esters, diethyl carbonate, dimethyl carbamoyl chloride, polymethylene polyphenylisocyanate, polycarbonate resins. Also used for manufacture of dyes, pesticides and herbicides.

Storage/transport conditions
Sold in rail tankers in quantities of 50 tonnes (liquefied gas under pressure).
67 sites are covered by Annex III of the Seveso directive (threshold 0.75 tonnes).

Reason for inclusion in Part 1 of Annex I
Based on generic criteria thresholds would be 5/20 tonnes ("very toxic"). Phosgene was not included in the original Commission proposal. It was proposed to keep this substance at the existing low threshold (0.75 t) for the higher level and to introduce an even lower threshold for the lower tier. Phosgene was thus included at 0.3/0.75 tonnes on the basis of this heavy gas' very low IDLH concentration, but also for political reasons.
Phosgene has been involved in 2% of the accidents reported in MARS up to and including 1993.

Arsine

Properties
Highly toxic, flammable, colourless gas (b.p. -62.5°C) of disagreeable garliac odour. Vapour density: 2.66.
It can react vigorously with oxidising materials and it may even explode when exposed to chlorine, nitric acid, or potassium plus ammonia. Container may explode in heat of fire. When heated, it decomposes and emits highly toxic fumes.
Arsine is one of the most powerful hemolytic poison encountered in industry. Signs of poisoning usually appear several hours after exposure. A human carcinogen.
LC50 inh rat: 390 mg/m^3/10 min. LCLo inh human: 25 ppm/30 min. IDLH: 6 ppm (19 mg/m^3).
Listed in Directive 67/548/EEC, Annex I, as "very toxic by inhalation" (R26), extremely flammable (R12), danger of serious damage to health by prolonged exposure by inhalation (R48/20), very toxic to aquatic organisms and may cause long term adverse effects in the aquatic environment (R50-53)".

Use
Arsine is used in the manufacture of electronic components and in organic syntheses. It may also be used as a poison gas for military purposes.

Storage/transport conditions
Stored in small quantities in cylinders (gas under pressure). Transport in tanks prohibited according to the ADR/RID agreement.
8 sites are covered by Annex III of the Seveso directive (threshold 0.01 tonnes).

Reason for inclusion in Part 1 of Annex I

Based on generic criteria thresholds would be 5/20 tonnes (“very toxic”). Arsine was not included in the original Part 1 Commission proposal, and suggestions were made to include arsine at considerably lower thresholds than it would have according to the generic criteria. Because of the very low IDLH concentration of this heavy gas, arsine was included at 0.2/1 tonnes.

Phosphine

Properties

Very toxic, flammable, colourless gas (b.p. -88°C) with disagreeable fishy or garlic-like odour. Vapour density: 1.17.

Phosphine is explosively hazardous when mixed with air. Container may explode in heat or fire.

The toxic effects are not fully understood. The chief effects are central nervous system depression and lung irritation. LC50 inh rat: 11 ppm/4h (0.016 mg/l/4h). LCLo inh human: 1000 ppm (after a few breaths). IDLH: 200 ppm (280 mg/m^3).

Based on LC50 inh. rat, phosphine is classified as “Very toxic by inhalation” according to criteria in Directive 67/548/EEC.

Use

It is used as a doping agent for solid state electronic components, as a polymerisation initiator and as a condensation catalyst. It is further used as an insecticide for fumigation of animal feed, leaf stored tobacco, box cars and for rodent control.

Storage/transport conditions

Stored in small quantities in cylinders. Transport in tanks prohibited according to the ADR/RID agreement.

8 sites are covered by Annex III of the Seveso directive (threshold 0.1 tonnes).

Reason for inclusion in Part 1 of Annex I

Based on generic criteria thresholds would be 5/20 tonnes (“very toxic”). Phosphine was not included in the original Part 1 Commission proposal, and it was suggested to include this substance at considerably lower thresholds than it would have according to the generic criteria. Although the IDLH is not extremely low, the LC50 inh. rat indicates that phosphine is about 30 times more toxic than the cut-off value for a “very toxic” substance. Phosphine was included at 0.2/1 tonnes.

Sulphur dichloride

Properties

Reddish brown fuming liquid with pungent chlorine odour (b.p. 59°C). Corrosive to skin, eyes and mucous membranes. Flammable when exposed to heat or flame. Reacts violently with e.g. water, ammonia, acetone, oxidants, metals. When heated to decomposition it emits toxic fumes of sulphur oxides and chloride.

Listed in Directive 67/548/EEC, Annex I, as “reacts violently with water (R14), corrosive, causes burns (R34) and irritating to respiratory system (R37)”.

Use

Rubber vulcanising, vulcanised oils, purifying sugar juices, sulphur solvent, chlorinating agent in metallurgy, manufacture of organic chemicals and insecticides.

Storage/transport conditions

Drums and tanks. 10 sites using sulphur dichloride are covered by Annex III of the Seveso directive (threshold 1 tonne).

Reason for inclusion in Part 1 of Annex I

Based on generic criteria thresholds would be 100/500 tonnes (“reacts violently with water”). Included at existing Annex III threshold (1 tonne).

Sulphur trioxide

Properties

Exists in three solid forms, the most valuable commercially is the γ form (m.p. 16.8°C) which has a strong tendency to polymerise to the straight chain β form, asbestos-like crystals, (m.p. 32.5°C) and subsequently to the cross-linked α form (m.p. 62°C). Solid transitions are commonly slow, a sample may be a mixture of the various forms and the melting point is not constant. The solids sublime easily. All forms boil at 45°C. At ambient temperatures in moist air it forms a white pungent mist. Sulphur trioxide is an oxidising agent. It is toxic by inhalation and corrosive to skin, eyes and mucous membranes. There is a fire risk in contact with organic materials. An explosive increase in vapour pressure occurs when the alpha form melts. Sulphur trioxide combines with water, forming sulphuric acid and evolving light and a large amount of heat. Violent reactions also with e.g. acetonitrile, formamide, dimethyl sulphoxide, iodine, metal oxides.
Not listed in Annex I to Directive 67/548/EEC.

Use

Sulphonation of organic compounds, especially nonionic detergents, and for solar energy collectors.

Storage/transport conditions

Drums and tanks. It is usually generated in the plant where it is to be used. 16 sites using sulphur trioxide are covered by Annex III of the Seveso directive (threshold 75 tonnes).

Reason for inclusion in Part 1 of Annex I

Based on generic criteria thresholds would probably be 100/500 tonnes (“reacts violently with water”). Several severe accidents involving sulphur trioxide have occurred in the past. Included at existing Annex II (art. 3/4) and Annex III thresholds (15/75 tonnes).
Sulphur trioxide has been involved in 1% of the accidents reported in MARS up to and including 1993.

Polychlorodibenzofurans and polychlorodibenzodioxins

Properties

There are 75 PCDDs and 135 PCDFs. The toxic and biochemical responses observed in laboratory animals experimentally exposed to PCDDs and PCDFs include, dermal (chloracne and related dermal lesions), immuno- and hepato-toxicity, carcinogenic, teratogenic and neurobehavioural effects, lethality, as well as numerous biochemical responses, such as the induction of several drug metabolising enzymes. Strong evidence exists that many of these effects are mediated by an aryl-hydrocarbon (Ah) receptor mechanism of action. The 2,3,7,8-substituted PCDD/F congeners ("congener" refers to any one particular member of the same chemical family, e.g. there are 75 congeners of chlorinated dibenzo-p-dioxins) are particularly potent in inducing Ah receptor-mediated toxic responses.

After the Seveso accident where about 2.5 kg of TCDD was released, chloracne was observed and other effects, like carcinogenic, teratogenic and mutagenic effects, are expected. 2,3,7,8-TCDD is one of the most toxic synthetic chemicals.

LD50 orl.rat: 20µg/kg, LD50 skin rabbit: 275 µg/kg.

Some of the PCDDs and PCDFs are extremely persistent in the environment. The half-life for 2,3,7,8-TCDD is first 1 year, then 10 years.

No PCDDs or PCDFs are listed in Annex I to Directive 67/548/EEC.

Sources and environmental occurrence

During many chemical reactions it has been found that PCDDs and PCDFs are formed as unwanted by-products. As a result many pesticides and technical products, including chlorophenols, chlorophenoxy herbicides and PCBs, have been contaminated with these compounds. The production and use of these chemicals are currently banned or strictly regulated in most countries. In the Seveso accident, TCDD was formed by a side reaction which occurred at an appreciable rate under abnormal conditions.

Other chemical processes generating PCDDs and PCDFs include the bleaching of pulp with chlorine and the production of graphite electrodes.

Combustion processes are considered to be an other important primary source of PCDDs and PCDFs. Most thermal reactions involving chlorinated organic or inorganic compounds result in the formation of PCDDs and PCDFs.

Of the 75 PCDDs and 135 PCDFs, usually only the 2,3,7,8-substituted congeners are present in biota. The absence of the non-2,3,7,8-substituted congeners can be explained by rapid metabolism and excretion of these congeners. In general, higher chlorinated congeners of 2,3,7,8-PCDD/Fs are more abundant than lower chlorinated compounds in most biotic samples and this is further accentuated in biota at higher trophic levels of the food chain.

In samples from combustion sources the profiles are generally not dominated by any particular congener group. In contrast, sample profiles from air, snow and sediment are strongly dominated by the hepta- and octa-chlorinated dioxins.

Reason for inclusion in Part 1 of Annex I

Emphasis has in the past been placed on 2,3,7,8-TCDD partly because it is the most potent representative of this class of compounds, and because it has been most often associated with human occupational exposure to the chlorinated phenols. However, the dioxins and dibenzofurans are structurally related and cause similar biological and toxicological effects by a similar mechanism. Thus “dioxin” should not be considered as a single entry; the isomers and related compounds in this group must be taken into account when human exposures are considered.

Many health organisations are currently estimating risks to humans in terms of the “dioxin equivalent” that is, the amount of the specific chemical or mixture which would cause the same degree of toxicity as 2,3,7,8-TCDD. Depending on the source of the mixture, health risks for exposure to the total equivalents from such sources may be many times that existing for TCDD alone from the same source.

In 1989 a group of the NATO-CCMS (Committee on the Challenges of Modern Society) worked out “the International Toxicity Equivalency Factor (I-TEF) method”, which is the result of the desire to achieve international consensus on factors to be used when assessing the toxicological significance of mixtures of PCDDs/PCDFs. This method is now used in Western Europe (one of the factors used in the Nordic countries differs from this method), USA and Canada.

WHO and IPCS (International Programme on Chemical Safety) are planning an update of the I-TEF method. The outcome of the updating is not expected to be revolutionary; the factors corresponding to some (very few) congeners might be changed.

Polychlorodibenzofurans and polychlorodibenzodioxins were included in the Seveso II proposal at 1kg, calculated as 2,3,7,8-TCDD equivalents using the International Toxicity Equivalency Factors, I-TEFs.

<u>Automotive petrol and other petroleum spirits</u>

Properties

Most petroleum types are complex mixtures that are difficult to characterise in detail, and therefore many definitions used to describe petroleum and its products lack precision, and terms can even be used in different ways by different sectors of the petroleum industry. Definitions of materials often are given in terms of the processes used to obtain them. Many petroleum products are blended, or modified from primary stocks as they come from the refining units. Trade names are not necessarily the refiner’s names, and one product may have more than one trade name, depending on the use.

Petroleum spirits (definition according to Sax and Lewis): benzine, benzoline, canadol, herbitox, ligroin, minaral spirits, mineral thinner, mineral turpentine, petroleum thinner, refined solvent naphtha, skelly-solve s, solvent naphtha, stoddard solvent, varnish makers’ and painters’ (VM&P) naphtha, varsol, white spirits.

Boiling point 40-80° C, flash point <-18° C. CAS: 64475-85-0.

Not listed in Annex 1 to Dir. 67/548/EEC under this number.

According to Kirk-Othmer, petroleum spirits are composed of straight-run naphtha, chemically treated, from paraffin-base or mixed-base crudes. Varnish makers’ and painters’ (VM&P) naphtha is reported to have a boiling range of 93-148°C.

In the UK “petroleum spirits” are generally defined as having an Abel flashpoint below 22.8 C.

Automotive petrol: includes regular leaded (blend of thermally or catalytically cracked, reformed or straight-run naphthas), premium leaded (blend of catalytically cracked, reformed, isomerised, and straight-run naphthas; alkylate) and unleaded (similar to premium leaded but without lead antiknock additives) grades in five volatility classes.

Use
Fuel and solvents.

Storage/transport conditions
Drums and tanks.

Reason for inclusion in Part 1 of Annex I
Based on generic criteria the thresholds would be 10/50 tonnes (“extremely flammable”). For pragmatic reasons (number of installations covered), automotive petrol and other petroleum spirits have been introduced in Part 1 at 5000/50000 tonnes (existing Annex II and III thresholds).

CARCINOGENS

The intention is that such carcinogens as are of particular concern after limited exposure and/or are very persistent in the environment should be listed. At the time being, no scientific criteria exist upon which the selection of such carcinogenic substances can be based. Information on effects on animals after short time exposure is very rare, since tests in general have been carried out in order to give information on the effects on workers, who are supposed to be exposed to these substances for long time periods. It should be noted that the classification of carcinogens according to Directive 67/548/EEC is based on how strong the evidence of causing cancer is and not on how potent a substance is.
Also information on environmental fate is rare. Determination of persistence in the environment and potential to accumulate in animals are based on test methods for biodegradability - respectively the distribution coefficient n-octanol/water and the bioconcentration factor. Information on solubility given for the carcinogenic substances below can be used as an indication on the distribution coefficient for n-octanol/water.

4-Aminobiphenyl and/or its salts

Properties

4-aminobiphenyl is a colourless crystalline solid, m.p. 53ºC and b.p. 302ºC. Slightly soluble in water but soluble in alcohol, ether and chloroform.

After long-time exposure, it produces cancer in mice, dogs and rabbits after oral intake, and liver tumours in mice after oral and intraperitoneal administration. The hydrochloride induces bladder and liver tumours in mice after oral administration. It is mutagenic to bacteria and mutagenic and DNA damaging in cultured mammalian cells. It induces bladder tumours in humans. No information available on effects to animals/man after short-time exposure, or environmental fate (except for solubility data above).

Listed in Directive 67/548/EEC, Annex I, as "carcinogen, cat. 1, may cause cancer (R45) and harmful if swallowed (R22)".

Use

It was manufactured as a rubber antioxidant but is no longer used. Marketing and use restricted to professional users.

Benzidine and/or salts

Properties

Benzidine (1,1'-biphenyl)-4,4'-diamine) is a white crystalline powder, m.p. 129ºC. It is only slightly soluble in water (0.4 g/l cold water) but soluble in ethanol and ether.

Benzidine and its salts have during long-time tests produced liver tumours by oral administration in rats, mice and hamsters, and bladder tumours in dogs. No adequate inhalation studies are available. It is mutagenic to bacteria, yeast and eukaryotic cells in culture. It also induced sister chromatid exchange, chromosomal aberrations and cell transformation in eukaryotic cells in culture. In vivo it induced DNA damage, sister chromatid exchanges, chromosomal aberrations and micronuclei. A causal relationship has been established in humans between exposure to benzidine and development of malignant tumours of the bladder. No information available on the effects to animals/man after short-time exposure, or environmental fate (except for solubility data above).

Benzidine and its salts are listed in Directive 67/548/EEC, Annex I, as "carcinogen, cat. 1, may cause cancer (R45), harmful if swallowed (R22), very toxic to aquatic organisms and may cause long term adverse effects in the aquatic environment (R50-53)".

Use

Benzidine was the basic starting chemical for a group of dyes. Now, these dyes are synthesised in other ways and benzidine is not used any more (banned), but exposure to benzidine can still occur due to release of benzidine as a breakdown product of dye.

Bis(chloromethyl)ether

Properties

Bis(chloromethyl)ether is a flammable liquid, b.p. 105°C. Soluble in alcohol and ether.

After long-time exposure, it is carcinogenic to rats and mice by inhalation, producing malignant nasal and lung tumours. Topical application produced local carcinomas to mice. It is mutagenic to bacteria and induces DNA damage in cultured human lymphocytes. There are strong indications that it induces lung cancer in humans.

No information available on effects to animals/man after short-time exposure, or environmental fate (except for solubility data above).

Listed in Directive 67/548/EEC, Annex I, as “carcinogen, cat. 1, may cause cancer (R45), very toxic by inhalation (R26), toxic in contact with skin (R24), harmful if swallowed (R22) and flammable (R10).

Use

It is widely used as a chloromethylating agent, particularly in the preparation of anion exchange resins and water repellents.

It is a contaminant (1-7%) of chloromethyl methyl ether.

Chloromethyl methyl ether

Properties

Chloromethyl methyl ether is a colourless flammable liquid, b.p. 59°C. Soluble in alcohol, ether, acetone and chloroform. Decomposes in water. Reported as biodegradable.

After long-time exposure, it (technical grade) may cause pulmonary and nasal cancer in rats and hamsters. It produced local sarcomas after subcutaneous injection in mice and was an initiator for mouse skin tumours. It is mutagenic to bacteria. In cultured cell assay systems it induced DNA damage and cell transformations. Occupational exposure to the technical grade is causally associated with an increased risk of respiratory cancer, mainly lung cancer. As the technical grade is contamined with bis(chloromethyl)ether, it is not possible to say if the effects are due to chloromethyl methyl ether itself, to the contaminant or to the combination. No information available on effects to animals/man after short-time exposure.

Listed in Directive 67/548/EEC, Annex I, as “carcinogen cat. 1, may cause cancer (R45), highly flammable (R11) and harmful by inhalation, in contact with skin and if swallowed (R20/21/22).

Use

It is widely used as a chloromethylation agent. The technical grade (which is the one used in industry) contains 1-7% bis(chloromethyl)ether.

Dimethylcarbamoyl chloride

Properties

Dimethylcarbamoyl chloride is a liquid, b.p. 165-167°C. It is rapidly hydrolysed.

After long time exposure, it is carcinogenic in rats and hamsters after inhalation, producing malignant tumours of the nasal cavity. Subcutaneous, intraperitoneal and skin exposures in mice induce malignant tumours at the site of treatment. It is DNA damaging and mutagenic to bacteria. In cultured mammalian cells it is mutagenic, clastogenic and induces sisterchromatid exchanges. In in vivo assay systems micronuclei were increased. There are no adequate epidemiological data to assess the carcinogenicity to humans. No information available on effects to animals/man after short-time exposure, or environmental fate.

Listed in Directive 67/548/EEC, Annex I, as "carcinogen cat.2, may cause cancer (R45), toxic by inhalation (R23), harmful if swallowed (R22) and irritating to eyes, respiratory system and skin (R36/37/38).

Use

It is used in the production of drugs and pesticides (highly reactive alkylating agent).

Dimethyl nitrosamine

Properties

Dimethyl nitrosamine is a yellow liquid, b.p. 154°C. It is soluble in water, alcohol and ether. No information available on environmental fate.

It is carcinogenic in many mammalian species after e.g. inhalation and ingestion, producing malignant tumours at various sites. In one study, tumours in the kidney and lung in mice were induced after administration of dimethyl nitrosamine in the drinking water (50mg/l) for one week. It is DNA damaging and mutagenic to bacteria and in cultured mammalian cells (where it also is cell transforming). In in vivo assay systems it is DNA damaging, clastogenic and it increases the frequencies of sister chromatid exchanges and micronuclei. Reported to be teratogenic in rats after single exposure. No adequate epidemiological data to assess the carcinogenicity to humans are available.

Listed in Directive 67/548/EEC, Annex I, as "carcinogen cat. 2, may cause cancer (R45), very toxic by inhalation (R26), toxic if swallowed (R25), danger of serious damage to health by prolonged exposure by oral intake (R48/25), toxic to aquatic organisms and may cause long term adverse effects in the aquatic environment (R51-53)".

Use

It used to be used for the production of liquid rocket fuel. Nowadays it is only used for research in mutagenicity and carcinogenicity. Exposure may for instance occur in environments where N-nitrosodimethylamine precursors, such as dimethylamine, come into contact with nitrosating agents such as nitrogen dioxide.

Hexamethylphosphoric triamide

Properties

Hexamethylphosphoric triamide is a water-white liquid, b.p. 230-232°C, soluble in water and polar and non-polar solvents.

After long-time exposure, it is carcinogenic in rats after inhalation, producing malignant tumours of the nasal cavity with a dose response relationship. It is not generally active in standard tests for DNA damage or mutations in bacteria. In cultured mammalian cells it is DNA damaging, mutagenic, clastogenic, increases sister chromatid exchanges and induces cell transformations. In in vivo assay systems micronuclei were increased and a dominant lethal test on mouse was positive. There are no epidemiological data to assess the carcinogenicity to humans. No information available on the effects to animals/man after short-time exposure, or environmental fate.

Listed in Directive 67/548/EEC, Annex I, as “carcinogen cat. 2, may cause cancer (R45), mutagen cat. 2, may cause heritable genetic damage (R46)”.

Use

It is used as a solvent for polymers, as a selective solvent for gases, as a polymerisation catalyst and as a stabiliser against thermal degradation in polystyrene.

2-Naphtylamine and/or salts

Properties

2-Naphtylamine is a white to faint pink solid (lustrous leaflets), m.p. 112°C, b.p. 306°C. It is soluble in hot water, alcohol and ether.

After long-time exposure, 2-naphtylamine is carcinogenic in mice, rats, hamsters, dogs and monkeys after oral administration, producing bladder tumours (and also liver tumours in mice). It is DNA damaging and mutagenic to bacteria. In cultured mammalian cells it is DNA damaging, clastogenic and increases sister chromatid exchanges. In in vivo assay systems the mouse coat spot test was positive and it induced mutations in Drosophila melangogaster, but it did not increase sister chromatid exchanges. Epidemiological data show that it induces bladder cancer in humans. There is no reason to believe that the salts of 2-naphtylamine will act differently since they are rapidly dissociated in the gastrointestinal tract. No information available on the effects to animals/man after short-time exposure, or environmental fate (except for solubility data above).

Listed in Directive 67/548/EEC, Annex I, as “carcinogen cat. 1, may cause cancer (R45), harmful if swallowed (R22), toxic to aquatic organisms and may cause long term effects in the aquatic environment (R51-53).”

Use

2-Naphtylamine was used as an intermediate in the production of dyes, but is no longer used. It may not be used in concentrations equal to or greater than 0.1% by weight in substances and preparations placed on the market. It is formed in the pyrolysis of nitrogen-containing organic matter (e.g. L-glutamic acid and L-leucine at 700°C).

1,3-Propanesultone

Properties

1,3-propanesultone is carcinogenic in rats after long-time oral administration and after one single intravenous injection, producing malignant tumours at various sites, including the brain. It is carcinogenic in the offspring of pregnant rats following one single prenatal intravenous injection, producing neurogenic tumours. Malignant skin tumours were developed in mice after a single application. It is DNA damaging and mutagenic to bacteria. In cultured mammalian cells it is DNA damaging, clastogenic and cell transforming. There are no data available to assess the carcinogenicity to humans.

No information available on environmental fate.

Listed in Directive 67/548/EEC, Annex I, as “carcinogen, cat. 2, may cause cancer (R45), harmful in contact with skin or if swallowed (R21/22)”.

Use

1,3-Propane sultone is an alkylating agent. It is used as a chemical intermediate to introduce sulphopropyl groups into industrial products such as detergents, wetting agents, cation exchange resins and the modified starches used in the textile industry.

4-Nitrobiphenyl

Properties

4-nitrobiphenyl is a light-yellow to reddish solid, m.p. 114°C, b.p. 340°C. It is insoluble in water, slightly soluble in cold alcohol and very soluble in ether.

There is inadequate evidence for the carcinogenicity to animals. In one long-time exposure test on 4 dogs (with no controls), bladder carcinomas were induced in 3 of them. Two other experiments in dogs were negative, but total dosages were low. It is DNA damaging and mutagenic to bacteria and cultured mammalian cells, and in the latter it also induced cell transformations. There are no epidemiological data available to assess the carcinogenicity to humans. It is possible that 4-nitrobiphenyl is carcinogenic by virtue of its (proposed) metabolic conversion to 4-aminobiphenyl.

No information available on the effects to animals/man after short-time exposure, or environmental fate (except for solubility data above).

Listed in Directive 67/548/EEC, Annex I, as “carcinogen, cat. 2, may cause cancer (R45)”.

Use

4-nitrobiphenyl was used as a chemical intermediate in the preparation of 4-aminobiphenyl, but is no longer used (banned).

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Appendix 1

Risk phrases according to Directive 67/548/EEC

R1	Explosive when dry
R2	Risk of explosion by shock, friction, fire or other sources of ignition
R3	Extreme risk of explosion by shock, friction, fire or other sources of ignition
R4	Forms very sensitive explosive metallic compounds
R5	Heating may cause an explosion
R6	Explosive with or without contact with air
R7	May cause fire
R8	Contact with combustible material may cause fire
R9	Explosive when mixed with combustible material
R10	Flammable
R11	Highly flammable
R12	Extremely flammable
R14	Reacts violently with water
R15	Contact with water liberates extremely flammable gases
R16	Explosive when mixed with oxidising substances
R17	Spontaneously flammable in air
R18	In use, may form flammable/explosive vapour-air mixture
R19	May form explosive peroxides
R20	Harmful by inhalation
R21	Harmful in contact with skin
R22	Harmful if swallowed
R23	Toxic by inhalation
R24	Toxic in contact with skin
R25	Toxic if swallowed
R26	Very toxic by inhalation
R27	Very toxic in contact with skin
R28	Very toxic if swallowed
R29	Contact with water liberates toxic gas
R30	Can become highly flammable in use
R31	Contact with acids liberates toxic gas
R32	Contact with acids liberates very toxic gas
R33	Danger of cumulative effects
R34	Causes burns
R35	Causes severe burns
R36	Irritating to eyes
R37	Irritating to respiratory system
R38	Irritating to skin
R39	Danger of very serious irreversible effects
R40	Possible risks of irreversible effects
R41	Risk of serious damage to eyes
R42	May cause sensitisation by inhalation
R43	May cause sensitisation by skin contact

R44	Risk of explosion if heated under confinement
R45	May cause cancer
R46	May cause heritable generic damage
R48	Danger of serious damage to health by prolonged exposure
R49	May cause cancer by inhalation
R50	Very toxic to aquatic organisms
R51	Toxic to aquatic organisms
R52	Harmful to aquatic organisms
R53	May cause long-term adverse effects in the aquatic environment
R54	Toxic to flora
R55	Toxic to fauna
R56	Toxic to soil organisms
R57	Toxic to bees
R58	May cause long-term adverse effects in the environment
R59	Dangerous for the ozone layer
R60	May impair fertility
R61	May cause harm to the unborn child
R62	Possible risk of impaired fertility
R63	Possible risk of harm to the unborn child
R64	May cause harm to breastfed babies