
Insight into Annex I



**Ministry of Environment and Water,
Bulgaria**

Structure of Annex I

- Part I - Categories of substances and preparations not specifically named in Part II
 - Based on generic toxicological, physical-chemical or ecotoxicological properties
 - Characteristic endpoints – LD₅₀, LC₅₀, EC₅₀, flashpoint, etc.
 - Part II – Named substances
 - Substances of high concern /TDI, Methyl isocyanide, phosgene, chlorine/
 - Widely used substances /ammonium nitrate, LPG, petroleum products/
 - Explanatory Notes
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Annex I – Named Substances

Substance	Threshold
Ammonium nitrate	10,000/5,000/2,500/50
Potassium nitrate	10,000/5,000
Chlorine	25
Ethylene oxide	50
Hydrogen	50
Toluene diisocyanate	100
Sulphur trioxide	75
Lead alkyls	50
Phosgene	0.75
Methyl isocyanate	0.15
Liquefied extremely flammable gases (including LPG) and natural gas	200
Petroleum products: gasolines and naphthas; kerosenes (including jet fuels); gas oils (including diesel fuels, home heating oils and gas oil blending streams)	25,000

Ammonium Nitrate

- ❑ Threshold – 10,000/5,000/2,500/50 t.
- ❑ Identification
 - CAS No – 6484-52-2
 - EC No – 240-827-6
- ❑ Hazard Classification
 - Oxidising, decomposes at 210°C, with evolution of toxic fumes of nitrogen oxides, it may explode under confinement and high temperatures, 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, ignites on contact with a number of substances, for instance sodium chloride.
- ❑ Uses
 - Production of fertilisers and explosives.

Potassium Nitrate

- ❑ Threshold – 10,000/5,000 t.
 - ❑ Identification
 - CAS No – 7757-79-1
 - EC No – 231-818-8
 - ❑ Hazard Classification
 - Strong oxidizer, Harmful if swallowed, May cause reproductive disorders.
 - ❑ Uses
 - Fertilizer, Food preservation, fire stabilizer, heat treatment of metals, Glass industry.
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Chlorine

- ❑ Threshold – 25 t.
 - ❑ Identification
 - CAS No – 7782-50-5
 - EC No – 231-959-5
 - ❑ Hazard Classification
 - Toxic by inhalation, Irritating to eyes, respiratory system and skin, Very toxic to aquatic organisms.
 - ❑ Uses
 - 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.
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Ethylene Oxide

- ❑ Threshold – 50 t.
 - ❑ Identification
 - CAS No – 75-21-8
 - EC No – 200-849-9
 - ❑ Hazard Classification
 - May cause cancer, May cause heritable genetic damage, Extremely flammable, Toxic by inhalation, Irritating to eyes, respiratory system and skin.
 - ❑ Uses
 - chemical intermediate for ethylene glycol (intermediate for the manufacture of polyester), 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.
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Hydrogen

- ❑ Threshold – 50 t.
- ❑ Identification
 - CAS No – 133-74-0
 - EC No - 215-605-7
- ❑ Hazard Classification
 - Extremely flammable
- ❑ Uses
 - 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 is used as coolant and missile fuel.

Toluene diisocyanate

- ❑ Threshold – 100 t.
- ❑ Identification
 - CAS No – 91-08-7, 584-84-9, 26471-62-5
 - EC No – 202-039-0, 209-544-5, 247-722-4
- ❑ Hazard Classification
 - Very toxic, Irritating to eyes, respiratory system and skin, Limited evidence of a carcinogenic effect, May cause sensitization by inhalation and skin contact, Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
 - Explosive in the form of vapour when exposed to heat or flame, when heated to decomposition it emits toxic fumes of nitrogen oxides.
- ❑ Uses
 - manufacture of polyurethane foams, elastomers and coatings. Crosslinking agent for nylon 6

Sulphur Trioxide

- ❑ Threshold – 75 t.
- ❑ Identification
 - CAS No – 7446-11-9
 - EC No – 231-197-3
- ❑ Hazard Classification
 - Oxidising agent, toxic by inhalation and corrosive to skin, eyes and mucous membranes, fire risk in contact with organic materials, 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.
- ❑ Uses
 - Sulphonation of organic compounds, especially nonionic detergents, and for solar energy collectors.

Lead Alkyls

- ❑ Threshold – 50 t.
 - ❑ Identification
 - Triethyl lead, tetraethyl lead and tetramethyl lead
 - ❑ Hazard Classification
 - toxic to the central nervous system, cumulative poison, experimental teratogens and have effects on reproduction, When heated to decomposition they emit toxic lead fumes.
 - ❑ Uses
 - used as octane enhancers for petrols, also in ethylation operations
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Phosgene

- ❑ Threshold – 0,75 t.
 - ❑ Identification
 - CAS No – 75-44-5
 - EC No – 200-870-3
 - ❑ Hazard Classification
 - Very toxic by inhalation, Causes burns.
 - ❑ Uses
 - 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.
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Methyl Isocyanide

- ❑ Threshold – 0,15 t.
- ❑ Identification
 - CAS No – 624-83-9
 - EC No - 215-605-7
- ❑ Hazard Classification
 - Highly flammable, Harmful by inhalation, Harmful in contact with skin, Harmful if swallowed. 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.
- ❑ Uses
 - intermediate in the manufacturing of N-methylcarbonate ester and N-methylurea insecticides and herbicides.

Liquefied extremely flammable gases (including LPG) and natural gas

- Threshold – 200 t.
- Identification
 - 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.
- Hazard Classification
 - Extremely flammable, Risk of fire and explosion.
- Uses
 - 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.

Petroleum products: gasolines and naphthas; kerosenes (jet fuels); gas oils (diesel fuels, home heating oils and gas oil blending streams)

- ❑ Threshold – 25000 t.
- ❑ Identification
 - Complex mixtures of hydrocarbons
 - Concawe Guidance Notes
- ❑ Hazard Classification
 - Flammable, Toxic for the environment
- ❑ Uses

 - Fuels and solvents

Annex I – Categories of substances and preparations

<i>PART I. Categories of substances and preparations not specifically named in Part II</i>		
No	Category	Threshold Quantity (metric tons)
1.	Flammable ²	50,000
2a.	Highly flammable ^{3(a) and (b)}	200
2b.	Highly flammable ^{3(c)}	50,000
3.	Extremely flammable ⁴	50
4.	Toxic ⁵	200
5.	Very toxic ⁶	20
6.	Oxidizing ⁷	200
7a.	Explosive, where the substance, preparation or article falls under Division 1.4 of the GHS criteria ⁸	200
7b.	Explosive, where the substance, preparation or article falls under Division 1.1, 1.2, 1.3, 1.5 or 1.6 of the GHS criteria ⁸	50
8a.	Dangerous for the environment – “Toxic to aquatic organisms” ⁹	500
8b.	Dangerous to the environment – “Very toxic to aquatic organisms” ¹⁰	200

Flammable

- ❑ *LIQUID* substances and preparations having a flash point equal to or greater than 21 °C and less than or equal to 55 °C, supporting combustion
 - ❑ Long chain and/or aromatic hydrocarbons and derivatives thereof
 - xylene, styrene
 - dibutyl ether
 - di-n-butylamine
 - ❑ About 130 entries in Classlab
 - ❑ Solvents, raw materials and intermediates in the chemical industry, paints, etc.
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Highly Flammable

- ❑ *LIQUIDS*
 - ❑ (a) Substances and preparations which may become hot and finally catch fire in contact with air at ambient temperature without any input of energy (are spontaneously flammable in air);
 - ❑ (b) Substances and preparations, which have a flashpoint lower than 55°C and remain liquid under pressure, where particular processing conditions, such as high pressure or high temperature, may create major accident hazards; and
 - ❑ (c) Substances and preparations having a flash point lower than 21°C and which are not extremely flammable.
 - ❑ Shorter chain and/or lower molecular mass liquids
 - carbon disulphide, heptane, toluene
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Extremely Flammable

- ❑ *Gaseous and Liquid State*
 - ❑ (a) Liquid substances and preparations which have a flash point lower than 0°C and whose boiling point (or, in the case of a boiling range, initial boiling point) at normal pressure is less than or equal to 35°C;
 - ❑ (b) Gases which are flammable in contact with air at ambient temperature and pressure, and which are in a gaseous or supercritical state; and
 - ❑ (c) Flammable and highly flammable liquid substances and preparations maintained at a temperature above their boiling point.
 - ❑ Gaseous methane, propane, butane, hydrogen, diethyl ether, ethylene oxide
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Toxic

- Substances with properties corresponding to those in table 1 or table 2 and having physical and chemical properties capable of creating industrial accident hazards

TABLE 1		
LD50(oral)(1)	LD50(dermal)(2)	LC50(3)
mg/kg body weight	mg/kg body weight	mg/l (inhalation)
25 < LD50 < 200	50 < LD50 < 400	0.5 < LC50 < 2

(1) LD50 oral in rats

(2) LD50 dermal in rats or rabbits

(3) LC50 by inhalation (four hours) in rats

TABLE 2
Discriminating dose mg/kg body weight = 5
where the acute oral toxicity in animals of the substance has been determined using the fixed-dose procedure

- About 420 entries into Classlab
- Endpoints - lethal dose or lethal concentration
- No single value – if differing LD50 values are available, take the lowest!
- It is up to the operator to prove hazardous properties

Very Toxic

- substances with properties corresponding to those in table 3 or table 4 and which, owing to their physical and chemical properties, are capable of creating industrial accident hazards

TABLE 3		
LD50(oral)(1)	LD ₅₀ (dermal)(2)	LC50(3)
mg/kg body weight	mg/kg body weight	mg/l (inhalation)
LD50 < 25	LD50 < 50	LC50 < 0.5

(1) LD50 oral in rats

(2) LD50 dermal in rats or rabbits

(3) LC50 by inhalation (four hours) in rats

TABLE 4
Discriminating dose mg/kg body weight < 5
where the acute oral toxicity in animals of the substance has been determined using the fixed-dose procedure.

- About 235 entries into Classlab
- Endpoints - lethal dose or lethal concentration
- No single value – if differing LD50 values are available, take the lowest!
- It is up to the operator to prove hazardous properties

Oxidizing

- ❑ substances which give rise to highly exothermic reactions when in contact with other substances, particularly flammable substances
 - ❑ About 235 entries into Classlab
 - ❑ Oxygen, peroxides, nitric acid
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Explosives

- ❑ (a) Substances or preparations which create the risk of an explosion by shock, friction, fire or other sources of ignition;
 - ❑ (b) Substances or preparations which create extreme risks of explosion by shock, friction, fire or other sources of ignition; or
 - ❑ (c) Substances, preparations or articles covered by Class 1 of the European Agreement concerning the International Carriage of Dangerous Goods by Road (UN/ADR), concluded on 30 September 1957, as amended.
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Explosives

- 2 subgroups
 - Explosive, where the substance, preparation or article falls under Division 1.4 of the GHS criteria – 200
 - Substances and articles which present only a slight risk in the event of ignition or initiation during carriage. The effects are largely confined to the package and no projection of fragments of appreciable size or range is to be expected. An external fire shall not cause virtually instantaneous explosion of virtually the entire contents of the package
 - Explosive, where the substance, preparation or article falls under Division 1.1, 1.2, 1.3, 1.5 or 1.6 of the GHS criteria – 50
 - Mass explosion, blast or projection hazard
 - Commercial and military explosives, detonators
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Dangerous for the environment – “Toxic to aquatic organisms”

- toxic to aquatic organisms with long-term adverse effects in the aquatic environment with:
 - (a) Acute toxicity:
 - (i) 96 hr LC50 (for fish): $1 \text{ mg/l} < \text{LC50} \leq 10 \text{ mg/l}$, or
 - (ii) 48 hr EC50 (for daphnia): $1 \text{ mg/l} < \text{EC50} \leq 10 \text{ mg/l}$, or
 - (iii) 72 hr IC50 (for algae): $1 \text{ mg/l} < \text{IC50} \leq 10 \text{ mg/l}$; and
 - (b) Persistency: the substance is not readily degradable or the $\log P_{ow}$ (log octanol/water partition coefficient) ≥ 3.0 (unless the experimentally determined bio-concentration factor BCF ≤ 100).
 - Over 800 entries in Classlab
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Dangerous to the environment – “Very toxic to aquatic organisms”

- (a) Substances very toxic to aquatic organisms, with acute toxicity:
 - (i) 96 hr LC50 (for fish) ≤ 1 mg/l, or
 - (ii) 48 hr EC50 (for daphnia) ≤ 1 mg/l, or
 - (iii) 72 hr IC50 (for algae) ≤ 1 mg/l
- (b) Substances very toxic to aquatic organisms with long-term adverse effects in the aquatic environment with:
 - (i) Acute toxicity:
 - 96 hr LC50 (for fish) ≤ 1 mg/l, or
 - 48 hr EC50 (for daphnia) ≤ 1 mg/l, or
 - 72 hr IC50 (for algae) ≤ 1 mg/l; and
 - (ii) Persistency: the substance is not readily degradable or the log Pow (log octanol/water partition coefficient) ≥ 3.0 (unless the experimentally determined bio-concentration factor BCF ≤ 100).

- Nearly 400 entries in Classlab
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