

# **HS428 At a Glance Look at the Dangerous Goods Classes Guideline**

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Policy Hierarchy link		Work Health and Safety Act 2011 Work Health and Safety Regulation 2011				
		Work Health and Safety Policy				
		Australian Dangerous Goods Code				
Respons	ible Officer	Director, UNSW Safety and Sustainability				
Contact	Officer	Manager, UNSW Health & Safety				
Superseded Documents		·				
File Number		2016/00370				
	Associated Documents		HS332 <u>Hazardous Chemicals Procedure</u>			
Associat			HS681 GHS Fact Sheet			
		HS716 Management of Picric Acid Protocol				
Version	Authorised by		Approval Date	Effective Date		
1.4	Director, UNSW Safety and Sustainability		23 March 2016	23 March 2016		

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# 1. Introduction and Scope

This guideline provides explanatory information relating to dangerous goods that should be read prior to the HS404 <u>Guideline for the Storage of Dangerous Goods</u>. Since the introduction of the Globally Harmonised System for the classification of Hazardous Chemicals, the term 'Dangerous Goods' is now mostly associated with transport. However, since the physical hazard classes in the GHS closely resemble similar classes in the Dangerous Goods class system the information below is valid for either classification system. See <u>GHS Fact Sheet</u> for more information.

# 2. Definitions

**Dangerous goods** are substances or articles that pose a risk to people, property or the environment, due to their chemical or physical properties.

**Explosive Precursors** are substances that can be used as ingredients in a mixture that could trigger an explosion.

**Cryogens** are gases that have been cooled such that they exist in their liquid phase (e.g. liquid nitrogen is stored at -196°C).

# 3. The 9 Classes of Dangerous Goods

There are 9 classes of dangerous goods which are defined by the Australian Dangerous Goods Code (ADG). The classification criteria used in the ADG is based on the United Nations Recommendations for the Transport of Dangerous Goods. Within some classes there are further divisions into sub classes e.g. within the Class 2 for Gases there are:

- I. Flammable gases (Class 2.1)
- II. Non-flammable, Non-toxic gases (Class 2.2)
- III. Toxic gases 2.3 (Class 2.3)

Other Classes are further divided into Packing Groups i.e.: Packing Group I (greatest danger), Packing Group II (medium danger) and Packing Group III (least dangerous).

The following is a brief summary of hazards and controls for each class of dangerous goods (excluding Class 6.2 Infectious Substances (See UNSW Bio-Safety procedure) and Class 7 Radioactive Substances (See UNSW Radiation Safety procedures)).



The Explosive Act (2003) and accompanying Explosives Regulation (2013) make it illegal to be in the possession of explosives or explosives pre-cursors without a license (in force since January 1<sup>st</sup> 2006). The only substance currently regulated as an explosive precursor is Security Sensitive Ammonium Nitrate (SSAN).

However, the Council of Australian Governments (COAG) has listed 11 priority chemicals (from a broader list of 96) as being 'precursor chemicals of a security concern'. These include various concentrations of the following chemicals:

- 1) Ammonium Perchlorate;
- 2) Hydrogen Peroxide;
- 3) Nitric Acid:
- 4) Nitromethane;
- 5) Potassium Chlorate:
- 6) Potassium Nitrate;
- 7) Potassium Perchlorate:
- 8) Sodium Azide;
- 9) Sodium Chlorate;
- 10) Sodium Perchlorate; and
- 11) Sodium Nitrate.

Extra vigilance is required for these chemicals in terms of maintaining control over the purchasing of such chemicals, maintaining their security during storage and rigorous stocktaking to ensure that such chemicals are not being removed from site for unauthorized activity. Further detail can be obtained from the <a href="Chemical Security">Chemical Security</a> website. In addition this website contains a full listing of all 96 'chemicals of a security concern'. The National Code of Practice for the Chemicals of Security Concern is available on this website; adherence to this is currently voluntary but highly recommended. In summary it requires vigilance for the acquisition and storage of all 96 chemicals to ensure their use is authorised and their storage is secure.

# Explosive and Unstable Chemicals that are not Class 1 Explosives

The following chemical groups are most commonly associated with explosions but are not Class 1 Explosives.

Acetylide	Hypohalitenitrate		
Amine Oxide	Nitrite		
Azide	Nitro		
Diazo	Ozonide		
Diasonium	Peracid		

Fulminate	Nitrogen Halides
Halates	Perhalates
n-Haloamine	Peroxides
Hydroperoxide	

Many chemicals are prone to react violently, either spontaneously or in contact with other incompatible materials. This often results in explosion or fire.

Risk management is essential to properly identify the hazards and explosive capability of these chemicals.

In managing the risks it is important to firstly identify whether your chemicals are:

- Friction or shock sensitive;
- Capable of strong exothermic reactions;
- Capable of producing unstable reactants;
- Touch sensitive detonators; etc.

Possible precautions could include:

- temperature control;
- safety screens;
- remote control operation;
- control of flow rates or degree of agitation; etc

A list of some Common Unstable Chemicals is listed in AS2243.2 Safety in Laboratories – Chemicals.

#### 3.2 Class 2: Gases



There are three sub classes within this class:

Class 2.1, the flammable gases can easily be ignited. Examples include Hydrogen, Acetylene, Methane and LPG.

Fire will result if the gases are present in a mixture with air such that they reach their flammable range. The following table lists some common flammable gases and their corresponding flammable range.

Gas	Flammability Range			
	LEL	UEL		
Hydrogen	4	75		
Acetylene	2	85		
Carbon Monoxide	12	75		
LPG	2.2	9.5		

Class 2.2 gases are inert but can displace Oxygen (i.e. asphyxiant gases). Such gases include Nitrogen, Helium and Carbon dioxide.

Gases can also possess subsidiary risks e.g. Oxygen is a class 2.2 gas with subsidiary oxidizing properties thus is labeled as Class 2.2/5.1.

Toxic gases belong to Class 2.3. These can have lethal effects at very low concentrations. Examples of toxic gases include: Carbon monoxide; Hydrogen sulphide; Silane.

# The Main Hazards of Class 2 Gases

(excerpts from AS:4332: The storage of Gases in Cylinders)

- Pressure: since they are stored in cylinders.
- Flammability: When mixed in the correct proportion with air, flammable gases will burn. If the concentration builds up in a confined space then an explosive mixture will form. Some gases e.g. H<sub>2</sub> will auto-ignite without needing a spark. Some gases have an odour added to detect if there is a leak e.g. LPG and acetylene.
- Reactivity: Some gases decompose and generate heat, e.g. acetylene.
- Toxicity: Toxic gases can cause damage either by inhalation or by contact with skin or eyes.
- Asphyxiation: Some gases may displace O<sub>2</sub> from the atmosphere. Any lowering of O<sub>2</sub> concentration to below 18% is dangerous. Asphyxiant gases, such as CO<sub>2</sub> and N<sub>2</sub>, may cause death if released in confined spaces e.g. cool rooms. An estimate of the oxygen concentration which would remain in the atmosphere of the room should there be a leak of an asphyxiant gas should be made assuming a complete container failure. Suitable safety devices such as oxygen monitors, including an alarm, may be required in certain situations.
- Oxygen enrichment: Too much O<sub>2</sub> in the atmosphere will increase the chance of a fire without there being an obvious fuel or ignition source.
- Temperature: When a gas cylinder is vented the change in pressure causes the gas to cool considerably. This may cause damage to people e.g. frostbite or any piping or equipment.

## Additional Hazards of Gases if involved in a Fire

Gases present the following specific hazards during a fire:

- Cylinders can rupture catastrophically.
- > Cylinders can become projectiles.
- > Cylinders can be knocked over by the pressure of water from a hydrant.
- > A released gas of Class 2.1 will feed a fire.
- A released gas having a subsidiary risk of Class 5.1 will make the fire burn more vigorously.
- A released gas of Class 2.3 can present a hazard to persons, and the turbulence and buoyancy associated with the fire could result in the dispersion of the toxic gas.
- Some Class 2.2 gases may release toxic fumes in a fire.
- Smoke and water run-off from fires may present a hazard to persons and the environment.

The appropriate Australian Standard to read for the safe handling of gases is "AS4332: The Storage and Handling of Gases."

Cryogenic gases are to be handled in accordance with "AS1894:The storage and handling of non-flammable cryogenic and refrigerated liquids."

# 3.3 Class 3: Flammable Liquids



Flammable liquids are classified on the basis of their flash points and boiling points. The flash point is the temperature at which the vapour from a flammable liquid becomes flammable.

Class 3 is further divided into three packing groups (PGs); PGI representing greatest danger.

The physical and chemical properties section on the SDS lists the important key indicators of flammability of these substances e.g. flash point, auto-ignition temperature, boiling point, lower explosive limits (LELs) and upper explosive limits (UELs).

The LEL is the % concentration of vapour in air below which, the material will not ignite. The UEL is the % concentration of vapour in air above which, the substance will not ignite. The range between the two is called the flammable range. Vapours form an explosive mixture in air within this range.

The following table is an example of 5 commonly used flammable liquids and the characteristics that earned them their dangerous goods class and packing group.

Substance	Flash Point °C	Auto Ignition temperature °C	Boiling Point °C	LEL %	UEL %	Packing Group
Carbon Disulphide	-30	90	46.3	1.3	50	I
Di-Ethyl Ether	-40	160	34.6	1.7	48	I
Ethanol	13	392	78	3.5	19	П
Acetone	-20	465-538	56	3	13	II
Xylene	27	500	138	1	7	III

The ease at which many commonly used flammable substances may be ignited and the spontaneous flammability of some of them may lead to serious incidents.

Containers holding flammable liquids need to be kept closed when not in use and work with flammable liquids should be conducted in a fume cupboard. This enables the vapours from the liquids to be safely extracted and directed away from potential ignition sources. Some substances are very volatile, meaning they can enter their vapour phase very quickly. They can be identified by having low boiling points and high vapour pressure. An example is Diethyl ether which is the main reason it is a packing group I substance.

The vapour from these volatile liquids can be readily transported around the room creating an obvious potential fire risk if ignition sources are present. Ignition sources include the obvious one such as Bunsen burners but they also include switches, pumps, hot plates and any other electrical devices. Anything which is capable of producing a spark can ignite the flammable vapour which will make its way back to the flammable liquid in its container, setting the contents alight. A fire can easily spread out of control if there are other sources of combustion present in the room (e.g. paper, boxes, other flammable liquids etc.).

Flammable liquids should never be heated by direct flame. Steam or water baths and

heating mantles must be used instead. Distillation operations involving flammable liquids require close and continuous attention. They should never be left unattended. Safety screens and face shields should be used when handling very reactive reagents or mixtures and all potential ignition sources should be removed.

As with all dangerous goods, maintain minimum stocks in the laboratory. Purchase in the smallest containers practicable and keep the largest quantities in a dedicated chemical store.

Flammable liquids must not be poured down the sinks. Many are lighter than water and immiscible with water. Vapours may travel through the plumbing system and flash back from an ignition source.

In laboratory upgrades or new facilities design, the use of spark proof electric fittings and intrinsically safe equipment may be required if large scale flammable liquid work is planned. Risk management planning will help with this determination.

The appropriate standard for flammable liquids is "AS1940: The Storage and Handling of Flammable and Combustible Liquids".

## 3.4 Class 4: Flammable Solids







There are 3 Sub classes of Flammable Solids: Class 4.1; Class 4.2; and Class 4.3.

#### 4.1 Flammable Solids

Flammable solids in powdered or finely divided form can form flammable or explosive mixtures with air. Some become flammable by:

- Friction or impact;
- Reaction with water or mist air;
- Contamination with combustible material:
- Decomposition on heating and exposure to sunlight.

Picric acid is a Class 4 flammable substance. It must be stored in >30% water. If it is allowed to dry out it becomes explosive. Contact the HS unit if you find bottles of picric acid that appear to have dried out. Management of this substance is required to follow HS716 Management of picric acid protocol and the HS717 picric acid inspection checklist.

Other flammable powdered metals are very dangerous: e.g. mixing powdered Aluminium and Iron Oxide (rust) into a mixture called "Thermite" will cause a reaction resulting in a temperature that can melt steel.

# 4.2 Substances liable to spontaneous combustion.

These substances are liable to spontaneous heating or can spontaneously combust in contact with air, and are then able to catch fire. Examples: Sodium Sulfide, *tert* butyllithium.

#### 4.3 Substances dangerous when wet.

These materials become spontaneously flammable or give off flammable gases in dangerous quantities. Example:  $CaC_2$  (calcium carbide) when wet will produce  $C_2H_2$  (acetylene).

Sodium metal is another example of a substance which is dangerous when wet and needs to be store under a hydrocarbon oil such as paraffin.

The appropriate standard for class 4 substances is AS/NZS 5026 The storage and

handling of class 4 dangerous goods. Users should also consult the individual SDS' for these substances.

# 3.5 Class 5: Oxidising Substances





This class is further broken down to Class 5.1 Oxidising Agents and Class 5.2 Organic Peroxides

<u>Class 5.1: Oxidising agents</u> are in themselves not necessarily combustible, but may cause or contribute to, the combustion of other material. Example: Sodium peroxide mixed with water will cause a strong exothermic reaction; mixing sodium peroxide with charcoal will spontaneously ignite. The appropriate standard is "AS4362: The Storage and Handling of Oxidising Agents."

<u>Class 5.2: Organic peroxides</u> are thermally unstable substances and may undergo a self-accelerating decomposition. They may also be liable to explosive decomposition, burn rapidly, be sensitive to impact or friction, and react dangerously with other substances.

The appropriate standard is "AS2714: The storage and handling of organic peroxides". Example: Benzoyl peroxide.

Organic peroxides are divided into 7 types depending on the level of their hazard:

- Types B, C, D, E, and F;
- Type A which is too dangerous to be transported; and
- Type G which is relatively harmless.

Organic peroxides can take any form: solid, liquid or paste.

# **Hazards of Class 5.2 Organic Peroxides**

Organic peroxides are notoriously reactive and unstable substances. Their specific chemical structure and their formulation (with additives or diluents) influence their degree of stability. They can react violently on exposure to friction, static electricity, contaminants and heat. The properties of organic peroxides require them to be stored in safe locations, at a temperature that is safe for each specific substance, away from sunlight and with appropriate segregation from other materials. A safety data sheet (SDS) should be obtained from the supplier for each specific organic peroxide that is stored.

#### Reactivity of Class 5.2 Organic Peroxides with other chemicals

Organic peroxides are violently reactive with the following incompatible materials (contaminants):

- strong acids and bases;
- resins;
- combustible material;
- oxidising and reducing agents;
- metals and metal compounds.

These contaminants accelerate the dissociation and decomposition of organic peroxides.

#### **Sensitivity of Class 5.2 Organic Peroxides to heat**

Because organic peroxides are sensitive to heat, careful attention needs to be paid to the temperature at which each specific substance is to be stored. The so-called 'self accelerating decomposition temperature' (SADT) of a specific organic peroxide is given in its SDS.

### **Health hazards of Class 5.2 Organic Peroxides**

Organic peroxides are toxic and may have a corrosive action on the skin, mucous membranes and eyes: in some cases corneal damage can be serious, even after brief contact.

# Storage and decanting of Class 5.2 Organic Peroxides

The following practices shall be strictly observed when storing, or decanting from, containers in minor storages:

- The containers must be stored on surfaces that are not liable to attack or damage by the contents if spilt.
- The containers need to be stored away from direct heat and ignition sources, e.g. hotplates, heating appliances, naked flames.
- ➤ Each organic peroxide must be stored below the maximum or recommended storage temperatures given in its SDS. Note that some organic peroxides require refrigeration during storage.

# **Summary Considerations for Class 5.2 Organic Peroxides**

Organic peroxides present certain specific hazards, as follows:

- > They may be flammable, toxic, corrosive or unstable.
- When heated, they may give off fumes or smoke, which may be flammable or toxic, or both.
- When contaminated, they may be highly unstable.
- They are sensitive to heat and may present a fire hazard. When subjected to excessive heating, they can decompose with evolution of more heat; in some cases the decomposition is accompanied by violent explosion.
- Some may react violently with other chemicals causing them to be sprayed over a wide area.
- Suitable non-combustible, inert absorbents, e.g. clean vermiculite or sand, must always be available where liquid oxidising agents are kept or handled. These absorbents must be clearly identified and stored in a laboratory spill clean-up kit.
- ➤ Equipment suitable for sweeping up leaks and spills of solid oxidising agents, and for sweeping up absorbent that has been used to absorb leaks and spills of liquid oxidising agents, e.g. a broom or brush, need to be located in the area where organic peroxides are stored.
- Clean, sealable (and where appropriate, vented) waste bins, made of plastic or other appropriate material compatible with the oxidising agents being dealt with, must be available for the containment of absorbed spills. It is advisable that such waste bins be filled to not more than two-thirds of their capacity. This waste requires special labelling to ensure that waste contractors are aware of the hazards.

Note: Some substances have the ability to form organic peroxides over time during storage e.g. Diethyl ether, (a Class 3 Flammable liquid). These substances take on the explosive capability of Class 5.2 Organic Peroxides. Such substances have expiry dates and must be either disposed of or rendered safe before this date has elapsed.

Substances which have this ability need to have the date they were purchased and first opened recorded on the label.

They need to be disposed of before the expiry date. Ensure that this information is recorded on the waste request form so that the contractors can prepare accordingly.

The list of 'Substances that can form Organic Peroxides' lists some substances that have expiry dates of 3 months and some that expire after 12 months. See also the section on Explosives which talks about common unstable chemicals, many of which belong to this class.

# Class 6: Toxic Substances



Class 6.1 Toxic Substances are substances liable to either cause death or serious injury or harm to human health if swallowed, inhaled or through skin contact.

Packing Group I substances have acute lethal effects meaning that if you are exposed to high concentrations of these substances for only a short period of time (this could be minutes), you could die unless someone removes you to fresh air immediately.

Toxic substances should be locked away to prevent access to unauthorised and untrained people.

All work with toxic substances should be conducted in the fume cupboard or, where this is impracticable (e.g. due to container sizes), in a suitable well ventilated area. A hazardous chemical weighing chamber should be considered for weighing out toxic material, depending on the risk.

Most carcinogens (substances with the potential to cause cancer), belong to this class 6 category of dangerous goods.

The International Agency for Research on Cancer (IARC), places substances into the following categories on the basis of their carcinogenicity:

Group 1: The agent (mixture) is carcinogenic to humans.

Group 2A: The agent (mixture) is probably carcinogenic to humans.

Group 2B: The agent (mixture) is possibly carcinogenic to humans.

Group 3: The agent is not classifiable as to carcinogenicity in humans.

Group 4: The agent is probably not carcinogenic to humans.

Many toxic substances are also labelled as Poisons under the Poisons and Therapeutic Goods Act and Regulation. Except for schedule 4 or schedule 8 drugs, the requirements for the use and storage of poisons are the same as for toxic substances. The additional requirements for schedule 8 drugs are outlined on the UNSW RECS website.

The appropriate standard to use is "AS4452: The Storage and Handling of Toxic Substances" Example: Sodium Cyanide (NaCN).

#### 3.7 Class 8: Corrosives



Corrosives are substances that, by chemical action, will cause severe damage when in contact with living tissue, or, in the case of leakage, will materially damage, or even destroy, other goods. Corrosives are further sub-divided into three packing groups based on their risk.

#### **Health Hazards of Class 8 Corrosives**

The primary health hazard presented by corrosive substances arises from their effect on human tissue. Damage to tissue can occur when the corrosive is in contact with the skin or eyes, or when swallowed or inhaled, Corrosive substances may also have toxic or oxidising properties. It is important to note that the corrosive effect of Class 8 substances on tissues may be delayed for some time before symptoms are detected. If treatment is delayed, this can add to the seriousness of injuries which result.

#### Other Hazards of Class 8 Corrosives

Depending on their nature, many corrosive substances can react with metals, with natural or synthetic fibres and with some other corrosive substances, e.g.: the reaction of inorganic acids with some metals leading to evolution of hydrogen; the reaction of sodium hydroxide with wool (the material is dissolved); the reaction between acids and bases. Some corrosive substances possess oxidising properties and can react with carbonaceous matter under certain conditions.

Incompatibility also exists between different substances within this class e.g. the reaction between some acids and bases and such substances should be segregated from each other during storage.

#### Clean-up materials and equipment for Class 8 Corrosives

In order to deal with leaks and spills (whether major or minor), clean-up equipment (including PPE), chemicals for neutralising or decontaminating spills and absorbent materials shall be maintained at every premises where corrosive substances are kept or handled. A typical list of appropriate items is as follows:

- Adequate quantities of absorbent material, eg. sand, fuller's earth or other absorbing substances;
- Calcium hydroxide (hydrated lime), for use on acidic spills;
- Sodium bisulphate, for use with alkaline spills;
- Crushed calcium carbonate (limestone);
- A sufficient number of re-sealable waste-recovery containers, e.g. drums, made of materials compatible with the substances being kept and appropriately marked as being for emergency use only;
- Approved containers made of appropriate materials, for the purpose of repackaging the contents of any leaking packages;
- Portable pumps and decanting equipment and shovels.

# Special note on Hydrofluoric acid (HF)

Hydrofluoric acid is one of the most corrosive of the inorganic acids. If it comes into contact with skin it will destroy the skin and subcutaneous destruction will commence. For concentrations greater than 48%, the pain on contact with skin can be immediately excruciating. At 10% concentration, no pain may be immediately felt but the destruction will continue. Any contact with HF, irrespective of concentration should receive treatment immediately.

Safe HF storage is essential and it should not be stored in any cupboard made from wood as it will destroy the wood. It will also corrode metal or glass shelving. Special corrosion resistance plastic is required.

Apart from a supply of running water, calcium gluconate gel **must be available** for first aid treatment. It must be located in the immediate area of use and storage.

All persons who work in a laboratory where HF is used must be properly informed of its hazards and required safety precautions.

The appropriate standard to use is "AS3780: The Storage and handling of Corrosive Substances".

# 4. References

All of the below standards are accessible from the Health & Safety website:

- AS 4332: The Storage and Handling of Gases in Cylinders
- ➤ AS 1894: The Storage and Handling of Non-Flammable Cryogenic and Refrigerated Liquids
- > AS 1940: The Storage and Handling of Flammable and Combustible Liquids
- ➤ AS 4326: The Storage and Handling of Oxidising Agents
- ➤ AS 2714: The Storage and Handling of Organic Peroxides
- ➤ AS/NZS 4452: The Storage and Handling of Toxic Substances
- ➤ AS 3780: The Storage and Handling of Corrosive Substances
- ➤ AS/NZS 5026 The storage and Handling of class 4 dangerous goods.
- ➤ AS 2243.2: Safety in Laboratories -Chemical Aspects

# **Appendix A: History**

Version	Authorised by	Approval Date	Effective Date	Sections modified
0.1	Director, Human Resources	1 November 2006	1 November 2006	Created 2 shorter guidelines from one original document. This guideline is an introduction to the 9 classes of dangerous goods. The second one focuses on the storage aspects of dangerous goods.
	Director, Human			Released for consultation purposes.  No changes from
1.0	Resources	1 January 2007	1 January 2007	consultation
1.1	Director, Human Resources	16 December 2010	16 December 2010	Updated Guideline to the standard University template.
1.2	Director, Human Resources	1 March 2013	1 March 2013	Updated with WHS Regulation 2011 Reference to the GHS system Minor grammatical and formatting Updated Branding Logo in accordance with UNSW Branding Guidelines. Modified the document identifier from OHS to HS in accordance with WHS legislation review
1.3	Director, UNSW Safety and Sustainability	30 April 2014	30 April 2014	Reviewed for administrative updates
1.4	Director, UNSW Safety and Sustainability	23 March 2016	23 March 2016	Reviewed for administrative updates