

Chemical Risk Management Protocol

Safe Methods of Use (SMOU)

Class 4 Reactive Solids

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1 Purpose

This Safe Method of Use (SMOU) applies to principal investigators (PIs), laboratory managers, designated laboratory persons (DLPs), and all staff and students who direct or participate in the use of UN Class 4 Reactive Solids at the University of Auckland.

Note: for pyrophoric materials please refer to **Safe Method of Use for Pyrophoric Solids**.

Pyrophoric materials shall only be handled by a chemist experienced in their use or under the supervision of an experienced chemist. The Safe Method of Use for Pyrophoric Solids must be followed.

Note: for picric acid please refer to **Safe Method of Use for Picric Acid**.

2 Disclaimer

Safety Data Sheet (SDS) Databases should be consulted for specific information about the compound you will be using. Gold FFX SDS Database is available on the Library database. Instructions on how to source this information can be found on the Health, Safety and Wellbeing Databases website:

<https://www.auckland.ac.nz/en/health-safety-wellbeing/health-safety-topics/laboratory-safety/chemical-safety/databases.html>

Please read this SMOU in conjunction with the Chemical Risk Management Guidelines.

Note: 'Shall' denotes a mandatory requirement and 'should' denotes a recommendation.

3 Classification

UN Class 4 solids are divided into three separate categories that must not be stored together. The corresponding HSNO and GHS7 classes are shown in the table below.

UN Class	HSNO Class	Corresponding GHS 7 Class
4.1 Flammable solids, self-reactive substances, polymerizing substances and solid desensitised explosives	4.1.1A/B	flammable solids Category 1-2
	4.1.2 A-G	self-reactive substances and mixtures Type A-G
4.2 Substances liable to spontaneous combustion	4.2A	pyrophoric liquids Category 1, or pyrophoric solids Category 1
	4.2B/C	self-heating substances and mixtures Category 2/3
4.3 Substances which, in contact with water, emit flammable gases	4.3A-C	substances and mixtures which, in contact with water, emit flammable gases Category 1-3

4 General Precautions for Storage

4.1 Segregation

HSNO Class 4 solids shall NOT be stored with HSNO Class 3 Flammable Liquids, HSNO Class 5.1 Oxidising Agents or HSNO Class 5.2 Organic Peroxides. In addition, HSNO Class 4.1, 4.2 and 4.3 chemicals are not compatible with each other, therefore shall be stored separately.

4.2 Water/Oil Immersion for Desensitisation

Those compounds that require water or oil immersion to remain stable shall be checked every 3 months to ensure there is sufficient covering liquid.

If reactive solids such as picric acid have been allowed to dry, please contact the University's Hazards and Containment Manager immediately.

These compounds may be extremely sensitive to any form of shock. DO NOT attempt to move the container or open the lid.

4.3 Water-sensitive chemicals

Water sensitive compounds shall be stored away from ANY source of moisture in dry and well-ventilated cabinets.

4.4 Monitoring

Those compounds that require water or oil immersion to remain stable shall be checked every 3 months to ensure there is sufficient covering liquid.

Containers of Class 4 chemicals shall be checked annually to ensure adequate containment.

5 General Precautions for Use of Class 4 Chemicals

- Ensure that these chemicals are used well away from any sources of ignition.
- Use these chemicals in a fume hood.
- Care should be taken when using reducing agents such as hydrides and borohydrides as they react violently with water.
- Safety glasses shall be worn when using these chemicals.

5.1 Use of pure alkaline metals

Use of pure alkaline metals should be restricted to laboratories within the School of Chemistry, the ACSRC, and Chemical and Materials Engineering. Other departments/schools will need to demonstrate that:

- Those handling the metals are suitably experienced in their use
- The laboratories to be used have the required equipment to facilitate safe use and storage.
- A risk assessment is performed before use.

6 Disposal

Disposal of HSNO Class 4 Reactive Solids shall be undertaken by a licensed chemical waste contractor.

Please contact the Chemical Safety Advisor for advice regarding disposal.

Each HSNO Subclass (i.e. 4.1, 4.2 and 4.3) shall be packed separately for disposal.

7 Spills

Consult SDS for correct clean up procedure

- Use correct gloves
- Solids can be placed directly impermeable/airtight container
- DO NOT USE WATER for HSNO Class 4.3 compounds
- Inform Laboratory Manager and arrange for immediate disposal

Appendix 1: Representative lists of Class 4 Chemicals

Note these lists are not exhaustive. Consult the SDS for correct classification.

HSNO 4.1.1. Flammable solids

Readily combustible solids (eg powders of metals and metal alloys) and solids which cause fire through friction (eg matches).

Borneol
Camphor, synthetic
2,4 Dinitrophenolhydrazine
Hexamethylenetetramine (methenamine)
Magnesium or magnesium alloys with more than 50% magnesium in pellets, turnings or ribbon
Metaldehyde
Naphthalene, crude or refined
Paraformaldehyde
Phosphorous, amorphous
Phosphorous pentasulfide
Phosphorous sesquisulfide
Phosphorous trisulfide
Silicon powder
Sulfur powder
Titanium powder
Trinitrobenzoic acid
Zirconium powder

HSNO 4.1.2. Self reactive substances

Compounds likely to undergo strongly exothermic reactions even without oxygen. The decomposition of these compounds can be initiated by heat, catalytic impurities (acids, heavy metal impurities or bases), friction or impact.

The following types of compounds tend to be self-reactive:

- a) aliphatic azo compounds ($R-N=N-R$)
- b) Organic azides ($R-N_3$)
- c) Diazonium salts ($R-N_2^+ X^-$)
- d) N-nitroso compounds ($-N-N=O$)
- e) Aromatic sulphohydrazides ($-SO_2-NH-NH_2$)

HSNO 4.1.3 Solid Desensitised Explosives

Those compounds which when wetted with water or alcohol or diluted with other substances to form a homogenous solid mixture, suppresses their explosive properties (eg Picric acid when wetted with more than 30% water)

Solid desensitised explosives listed here are explosive if allowed to dry!

4.1.3A - Solid desensitised explosive (High Hazard)

Substance	Minimum percentage water to be added
2-amino 4,6 dinitrophenol	20%
Ammonium picrate	10%
Barium azide	50%
2,4-Dinitrophenol	15%
2,5-Dinitrophenol	15%
2,6-Dinitrophenol	15%
Dinitroresorcinol	15%
Nitroguanidine	20%
Dipicryl sulfide	10%
Picric acid (2,4,6 Trinitrophenol)	30%
Picramide (Trinitroaniline)	30%
Picramic acid (2 amino-4,6 dinitrophenol)	30%
Silver picrate	30%
Sodium dinitro-o-cresolate	15%
Sodium picramate	20%
2,4,6 Trinitrobenzene	30%
2,4,6 Trinitrotoluene	30%
Urea nitrate	20%
Zirconium picramate	20%

4.1.3B - Solid desensitised explosive (Medium Hazard)

Azodicarbonamide
Isosorbide dinitrate mixture with not less than 60% lactose, mannose, starch or calcium hydrogen phosphate
Nitrocellulose with alcohol, not less than 25% alcohol by mass and not more than 12.6% nitrogen by dry mass
Nitrocellulose with not more than 12.6% nitrogen by dry mass, mixture with or without plasticizer, with or without pigment
Nitrocellulose with water, not less than 25% water by mass
Pentaerythrate tetranitrate

HSNO Class 4.2 - Spontaneously Flammable Substances

Spontaneously flammable substances are those which are:

1. Pyrophoric [which even in small quantities ignite within 5 minutes of coming in contact with air]
2. Self-heating [will ignite only when in kilogram amounts or after long periods of time (hours or days)]

Examples include:

Organolithium reagents, e.g. n-butyllithium

Metal hydrides, e.g. sodium hydride, lithium aluminium hydride, Diisobutylaluminum hydride

Grignard reagents, e.g. Isopropylmagnesium chloride, methylmagnesium bromide

Activated carbon

Diethyl zinc

Sodium hydrosulfide

Sodium methoxide

Sodium sulfide

Titanium powder

Tri-n-butylphosphine

HSNO Class 4.3 - Solids which are dangerous when wet

Substance	HSNO Classification (Category A is most hazardous)
Aluminium powder, coated	4.3B
Aluminium powder, uncoated	4.3B
Aluminium Tert-Butoxide	4.3B
Barium	4.3B
n-Butyl lithium	4.3B
Calcium	4.3B
Calcium carbide	4.3A
Calcium cyanamide	4.3C
Calcium hydride	4.3A
Calcium phosphide	4.3A
Lithium	4.3A
Lithium Aluminium hydride	4.3A
Lithium borohydride	4.3A
Lithium hydride	4.3A
Magnesium Powder	4.3A
Phosphorous pentasulfide	4.3A

Potassium	4.3A
Potassium Borohydride	4.3A
Rubidium	4.3A
Silicon powder, amorphous	4.3A
Sodium	4.3A
Sodium Borohydride	4.3A
Sodium Hydride	4.3A
Sodium phosphide	4.3A
Stannic phosphide	4.3A
Thiourea Dioxide	4.3A
Zinc powder or dust	4.3A
Zinc powder, pyrophoric	4.3A