

Safe Method of Use 11

HSNO Class 4 - Reactive Substances

Purpose: This Safe Method of Use applies to **principal investigators (PIs), sector managers, designated laboratory person (DLPs)**, technical staff and students who use laboratories within the University of Auckland.

Please refer to **Safe Method of Use for Highly Hazardous Compounds – Safety Guidelines for Pyrophoric Solids.**

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

Note: ‘Shall’ denotes a mandatory requirement and ‘should’ denotes a recommendation.

A. Classification

HSNO Class 4 solids are classified into three separate UN Categories

- HSNO Class 4.1 - Flammable solids, self-reactive substances and solid desensitised explosives
- HSNO Class 4.2 - Substances liable to spontaneous combustion
- HSNO Class 4.3 - Substances which are dangerous when wet

B. Incompatibilities

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.

C. General Precautions for Storage

1. 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.

2. Those compounds that require water or oil immersion to remain stable **shall** be checked every 3 months to ensure there is sufficient covering liquid.
3. If reactive solids such as picric acid have been allowed to dry please contact the University Hazards and Containment Manager immediately.
4. ***These compounds may be extremely sensitive to any form of shock. DO NOT attempt to move the container or open the lid.***
5. Use of pure alkaline metals **should** be restricted to laboratories within the Department of Chemistry and the ACSRC.
6. Water sensitive compounds **shall** be stored away from ANY source of moisture in dry and well ventilated cabinets.

D. General Precautions for Use

1. Ensure that these compounds are used well away from any sources of ignition.
2. Use these compounds in a fume hood.
3. Care should be taken when using reducing agents such as hydrides and borohydrides as they react violently with water.
4. Safety Glasses **shall** be worn when using these compounds.

E. Limits on Storage Time

1. Those compounds that require water or oil immersion to remain stable **shall** be checked every 3 months to ensure there is sufficient covering liquid.
2. Containers of Class 4 chemicals **shall** be checked annually to ensure adequate containment.
3. If reactive solids such as picric acid have been allowed to dry please contact the University 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.

F. Disposal

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

2. Please contact Hazards and Containment Manager to arrange for disposal.
3. Each HSNO Subclass (i.e. 4.1, 4.2 and 4.3) **shall** be packed separately for disposal.

G. Spills

1. Consult MSDS for correct clean up procedure
2. Use correct gloves
3. Solids can be placed directly impermeable/airtight container
4. DO NOT USE WATER for HSNO Class 4.3 compounds
5. Inform Laboratory Manager and arrange for immediate disposal

Appendix: List of Representative Class 4 Compounds

HSNO Subdivision of 4.1 Compounds

HSNO Class 4.1 compounds have been assigned 3 major HSNO Categories:

- 4.1.1 - Readily Combustible compounds
- 4.1.2 - Self-reactive compounds
- 4.1.3 - Solid desensitised explosives

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)

Representative List of Class 4.1.1 Compounds

Aluminium powder
Azobisisobutyronitrile
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 (-C-N=N-C-)
- b) Organic azides (-C-N₃)
- c) Diazonium salts (-CN₂⁺Z⁻)
- d) N-nitroso compounds (-N-N=O)
- e) Aromatic sulphonylhydrazides (-SO₂-NH-NH₂)

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 suppress their explosive properties (eg Picric acid when wetted with more than 30% water)

A Representative List of HSNO 4.1.3A - Solid desensitised explosives (High Hazard)

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

Substance	Minimum Percentage water that compound to be wetted
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

4.1.3C - Solid desensitised explosive (Low Hazard)

5-tert-Bulyl-2,4,6-trinitro-m-xylene

2-bromo-2-nitropropane-1,3-diol

Isosorbide-5-mononitrate

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)]

Activated carbon

Boron trifluoride dimethyl etherate

Camphene (Bicycloheptane, 2,2-Dimethyl-3-Methylene)

Diethyl zinc

Nitronaphthalene

p-nitrosodimethylaniline

Pentaborane

Phosphorus, amorphous

Potassium Dithionite (Potassium hydrosulphite)

Potassium sulfide

Sodium dithionite (Sodium hydrosulphite)

Sodium hydrosulfide

Sodium sulfide

Sodium Methylate (Sodium methoxide)

HSNO Class 4.3 - Solids which are dangerous when wet

Substance	HSNO Classification
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