Chemical Risk Management Protocol

Safe Methods of Use (SMOU)

Working with Potentially Explosive Chemicals/Reactions

Table of Contents

1 Purpose

This Safe Method of Use (SMOU) applies to principal investigators (PIs), laboratory managers, designated laboratory person (DLPs), and all staff and students who direct or participate in the use of chemical reactions with explosive potential at the University of Auckland.

2 Disclaimer

This SMOU should be used as guidance to inform a risk assessment that considers all aspects and potential hazards related to the use of the chemical. **Please read this SMOU in conjunction with the Chemical Risk Management Guidelines.**

The Safety Data Sheet (SDS) should be consulted for specific information about the chemical you will be using. The 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

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

See Appendix 1 for a representative list of explosive and potentially explosive chemicals.

3 General Guidelines

1. While every care must be taken to ensure chemical reactions do not proceed in an uncontrolled manner, some chemical reactions carry a risk (however small) of becoming uncontrolled resulting in splash or burst hazard or in rare cases an explosion.
2. Prior to conducting the experiment, laboratory workers shall consult the experimental procedure and adhere to any advised cautions, particularly where

blast shields are recommended. Laboratory workers shall also consult closely with their supervisor.

3. Ensure there are no unnecessary flammable/reactive solvents/materials in the fume cupboard when a potentially explosive reaction is being conducted.
4. Unattended experiments must be clearly labelled to identify possible hazards and steps to take in case of an incident.
5. There are two main sources of protective barrier available to protect laboratory personnel in such events – a blast shield and the fume cupboard sash.
   - Blast shields can be moved into the fume cupboard for the duration of the experiment.
   - Fume hood sashes are designed to be lowered to provide a physical barrier between reaction in the fume hood and laboratory personnel.

Note: **Most explosions occur while purifying or distilling mixtures. Therefore, use extreme caution before concentrating or purifying any mixture that may contain an explosive chemical** (e.g. a peroxide-forming chemical or azide)**.**

4 PPE

- Laboratory workers (Student/Staff) shall wear and have access to full face shields when;
  - blast shields have to be removed to manipulate glassware that has not cooled to room temperature
  - At any time where the Lab worker’s face may be exposed to an explosive reaction even with a blast shield in place.
- When a full face mask is used, safety glasses shall be worn in addition.

5 Protective Barriers and their Use

5.1 Blast Shields

Use of blast shields is mandatory at all times for the following reactions:

- Reactions where there is a clearly stated explosion hazard for either reactants or products (e.g. IBX) or where reactants /products are those listed in Appendix 1 – Explosive and Potentially Explosive Chemicals
- Any reactions involving diazonium compounds, diazomethane, highly nitrated compounds and when heating organic peroxides.
- Reactions involving strong oxidising agents in quantities greater than 500 mL.
- Reactions involving strong reducing agents (such as Lithium Aluminium hydride) in quantities greater than 10 g of reagent.

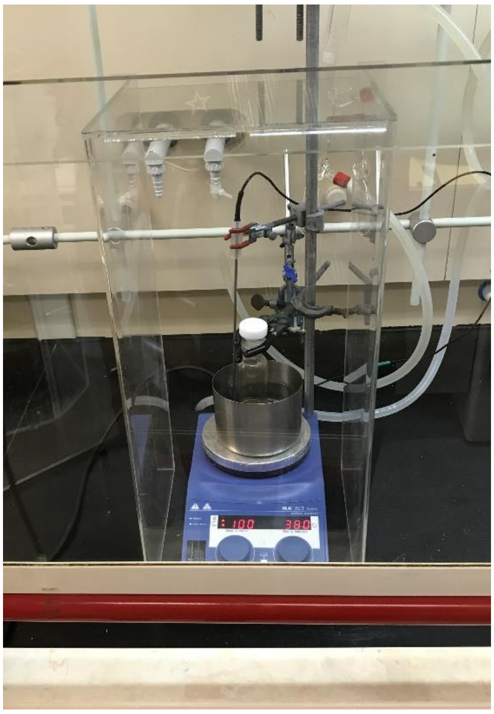

Figure 1: Ideal use and set up of a blast shield. Note that the combination of fully lowered fume hood sash and blast shield assist in containing any potential explosion.

5.2 Fume hood sashes

Fume hood sashes shall be lowered to the fullest extent when the following procedures are being carried out:

- Reactions involving chemicals listed in Appendix II
- Large scale distillations.

Any faults or observed lack of airflow in the fume hood when the fume hood sashes are lowered shall be reported to the Laboratory Manager immediately.

6 Potentially Explosive Chemicals (PECs) and Reactions

Explosive chemicals can release tremendous amounts of destructive energy rapidly. If not handled properly, these chemicals can pose a serious threat to the health and safety of laboratory personnel, emergency responders, building occupants, chemical waste handlers, and disposal companies. For example, an explosion of old isopropyl ether killed a laboratory worker when he attempted to remove a glass stopper from the container. In another instance, tetrazole exploded inside a hazardous waste incinerator, causing major damage and costly repairs.

Most chemicals that are used in research and teaching laboratories are stable and non-explosive at the time of purchase. Over time, some chemicals can oxidise, become contaminated, dry out, or otherwise destabilise to become PECs (e.g., sodium amide, picric acid and peroxidizable organic chemicals such as isopropyl ether). See **Appendix I Explosive and Potentially Explosive Families** for examples. For additional information, please refer to the SMOUs for Picric acid and Peroxide-forming chemicals.

Unlike known explosives, which are designed to be stable under normal conditions, PECs are particularly dangerous because they may explode if they are subjected to heat, light, friction, or mechanical shock.

6.1 Common Laboratory PECs

The following are some commonly used chemicals in academic research laboratories that can become an explosion hazard under certain conditions:

- Organic chemicals that form peroxides through exposure to air or light, such as diethyl ether, diisopropyl ether, tetrahydrofuran (THF). Please refer to SMOU Peroxide-Forming Chemicals for more examples of these.
- Hydrated picric acid that becomes dry or becomes contaminated with metals that form metal picrate salts.
- Sodium amide that reacts with air or moisture to form superoxides, as evidenced by yellow or brown discoloration.
- Certain alkyl nitrates (e.g., butyl nitrate or propyl nitrate) that become contaminated with nitrogen oxides.
- Certain normally stable perchlorates (e.g., pyridinium perchlorate or tetraethylammonium perchlorate) that become unstable at elevated temperatures.
- **Azides** (*see* **Section 6.2 below**). This includes general organic azides (especially those of molecular weight <200), metal azide complexes, diazotransfer reagents and organic azides used in click chemistry.

6.2 Azides | Compound assessment and safe use

Azides represent a class of PECs that require specific risk assessment and training for safe use. Due to their usefulness in a range of important reactions they have many possible applications, but workers must be aware of the potential hazards and risk mitigation strategies. Before using azides, users must be adequately trained and follow their department/school procedures regarding azide use. For example, in the School of Chemical Sciences, SCS Canvas azide training and PI signoff are **mandatory** before starting any experimental work. Work on the smallest feasible scale with any azides.

Quenching of azides

This can be carried out if determined by PI to be a viable alternative to disposal via marked waste containers.

HN_3 or N_3^- can be quenched by nitrous acid:

$$2NaNO_2 + H_2SO_4 \rightarrow 2HNO_2 + Na_2SO_4$$

$$2NaN_3 + 2HNO_2 \rightarrow 3N_2\ (g) + 2NO\ (g) + 2NaOH$$

This operation should only be carried out in a fume hood using a vessel with a gas outlet:

1 In a three-neck flask with a stirrer, dilute the azide with water so that it does not exceed 5%

2 With stirring add a solution of sodium nitrite containing 1.5 g of sodium nitrite per gram of excess azide

3 Add 2-3M H_2SO_4 dropwise (on small scale, by pipette; on large scale, using a dropping funnel) until gas evolution has ceased and the solution is acidic by test paper.

Iodide-starch paper can be used to test for an excess of nitrite (goes blue) which indicates that the quench is complete. Dispose of the solution as you would other aqueous waste.

Azides fall into several categories that warrant separate consideration;

Azide class	*Safety considerations*
Sodium azide CAS 26628-22-8	*Highly toxic through skin contact, inhalation, and ingestion.* Must be used according to the SMOU for Class 6 Toxic Chemicals. Aqueous waste should be collected in a separate, labelled container and sent for disposal. pH of waste must be checked and maintained as basic (7-9) to avoid formation of hydrazoic acid.
Metal azides	Inorganic azides are explosive under certain conditions and should be treated as PECs; handled carefully, protected from light, shock, and heat. Avoid contact with metal spatulas or components. Avoid contact with chlorinated solvents or acid. Evaporated mixtures of metal azides and organic compounds should be treated as PECs.
Organic azides	Each chemical you intend to work with must be individually evaluated. Stability of organic azides generally depends on the number of carbon atoms present. **Compounds with C/N > 3** can be handled safely but the guide for safe working procedures for PECs should be followed. **Compounds with C/N 2-3** can be made but require PI signoff and extreme care under safe working procedures for PECs. Some literature examples (*e.g.* phenyl azide) are documented. Compounds should be stored as solutions and evaporation to dryness avoided where possible. Avoid contact with chlorinated solvents or acid. **Compounds with C/N < 2** should only be used as solutions and evaporation to dryness avoided where possible. Transient formation of azides with C/N <3 as reaction intermediates may be done safely, keeping the maximum possible quantity under 1 g, as long as the intermediate is expected to be consumed during the reaction, and this can be monitored. *See flowcharts on following page for assessment of azide compounds*
Hydrazoic acid CAS 7782-79-8	Highly explosive when neat. Avoid formation in aqueous azide waste streams by treatment with aqueous base, or on surfaces with soap-water wash.

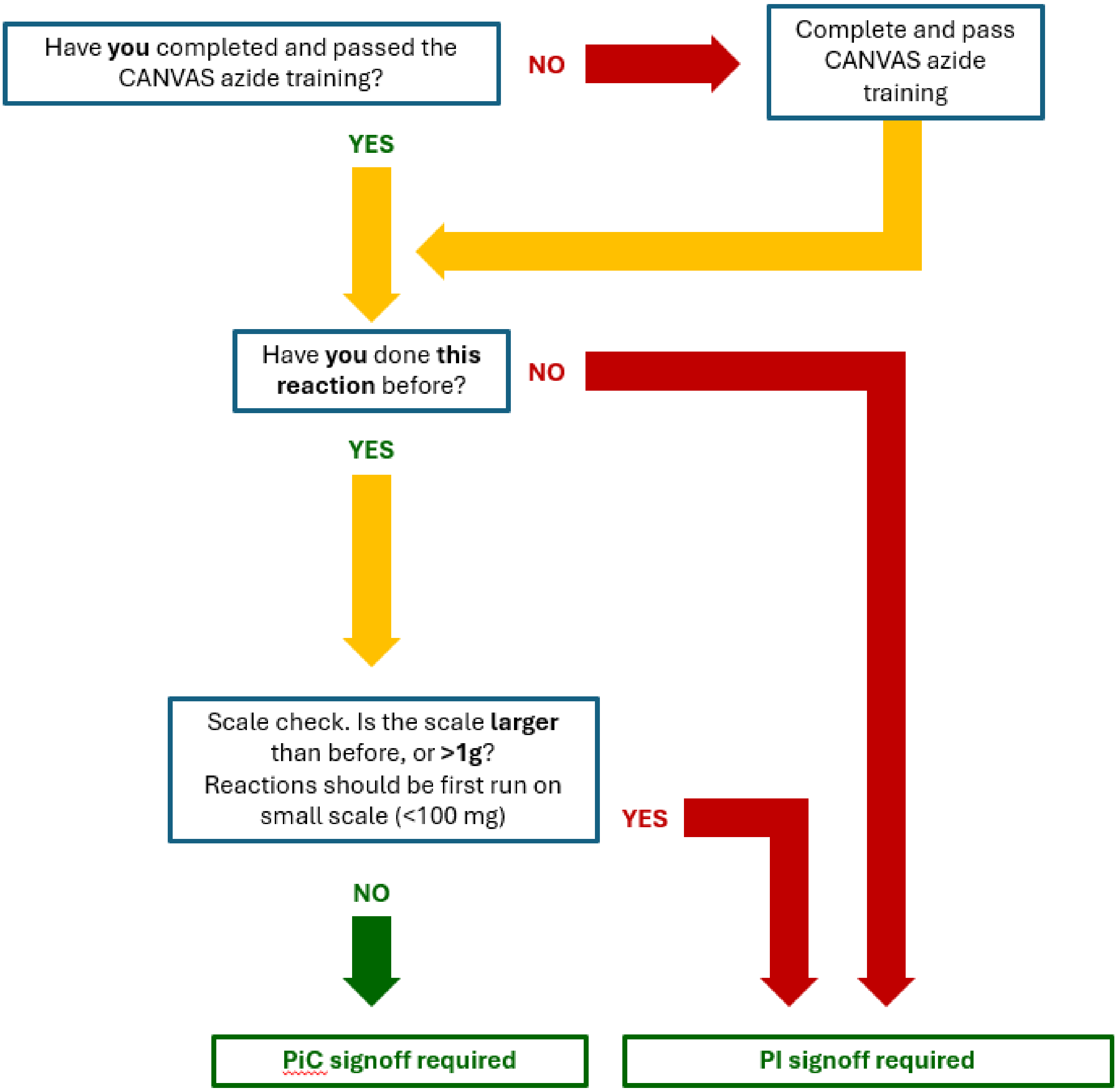

Figure 2: Flowchart for assessment of azide compounds prior to use, as used in the School of Chemical Sciences

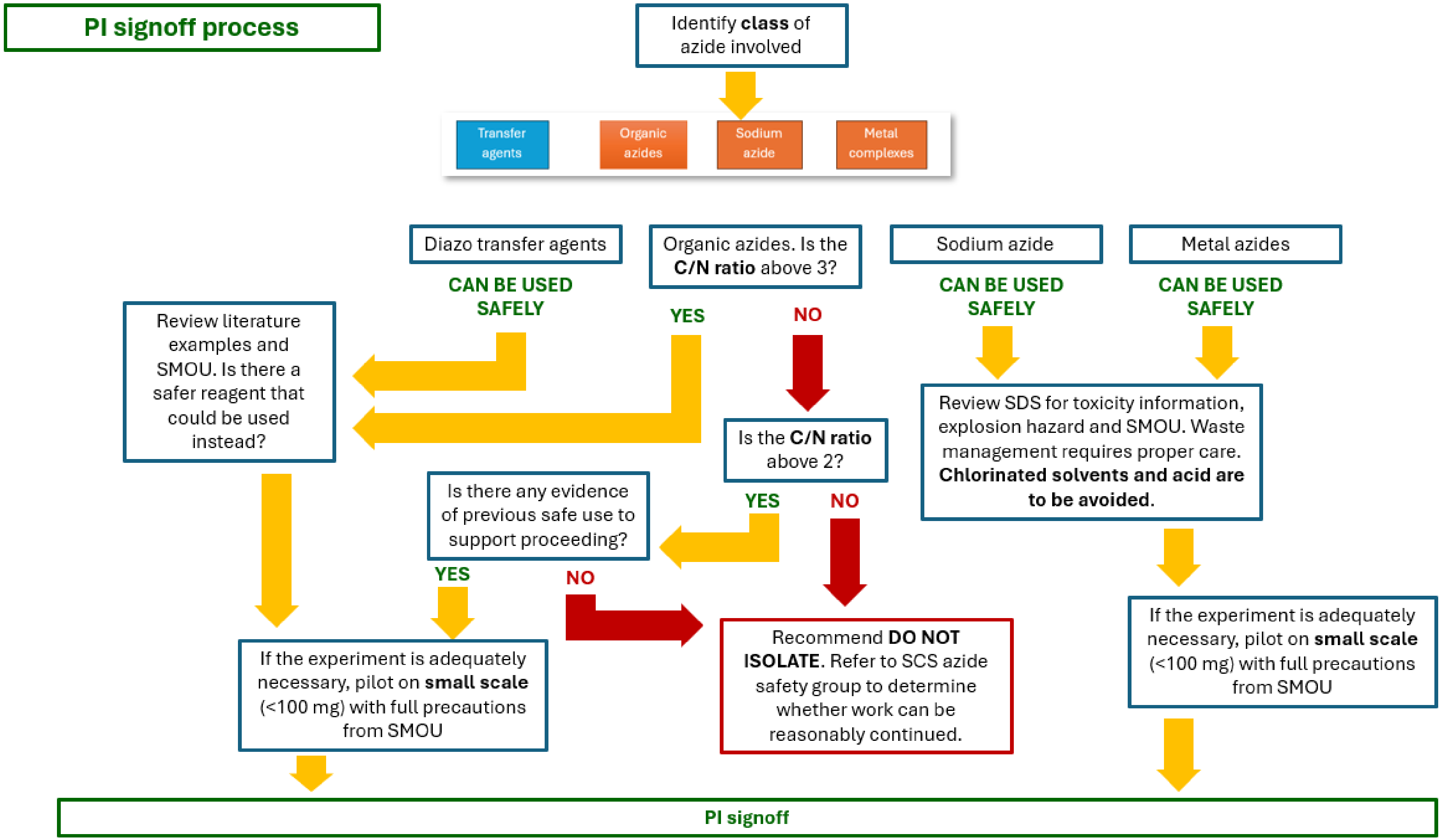

Figure 3: Flowchart for PI Signoff Process as used in the School of Chemical Sciences

6.3 Chemicals that can become explosive during storage

There is an additional group of chemicals that should be considered although they are not necessarily heat-, light-, friction-, or shock-sensitive. These chemicals give off gaseous degradation by-products that may cause over-pressurisation of the container and explode. They can degrade over time and should be incorporated into a safety and handling system that will prevent them from becoming explosive hazards.

Please see **SMOU Management of Time-Sensitive Chemicals** for more information.

For example:

- Highly concentrated formic acid (>90%) can decompose upon prolonged storage to form carbon monoxide gas. The formation of gas can cause explosion of the container. Containers should have self-venting caps; dispose of any that are old and do not have these.
- Nitric acid waste is a common cause of lab explosions, when it is mixed with incompatible chemicals such as acetone, formic acid, or other flammable organic solvents and sealed.
- See Appendix II for additional examples.

6.4 Potentially explosive reactions

Heating large amounts of flammable solvents (≥500 mL) under reflux poses an increased risk of ignition or explosion. Such experiments shall not be left unattended.

Appendix I: Explosive and Potentially Explosive Chemical Families

The following table lists classes of PECs, with some examples for each class. Please note this is not an exhaustive list; consult the SDS for details about the specific chemicals you are using.

Azides Hydrogen azide	**Metal Azide Halides** Chromyl azide chloride Molybdenum diazide tetrachloride Tungsten azide pentachloride
Metal Azides Aluminum azide Bis(cyclopentadienyl)tungsten diazide oxide Mercury (I&II) azide Lead azide Sodium azide	**Organic Azides** Diazidomethyleneazine Picryl azide Vinyl azide Acetyl azide Cyanodiazoacetyl azide Phenylphosphonic azide chloride
Diazo compounds 2-Buten-1-yl diazoacetate Diethyl diazomalonate Dinitrodiazomethane Diazomethane	**Diazonium carboxylates, perchlorates, salts, sulfates, tetrahaloborates, and, triiodides** Benzenediazonium-2-carboxylate 4-Aminobenzenediazonium perchlorate 6-chloro-2,4-dinitrobenzenediazonium sulfate 2-Nitrobenzenediazonium tetrachloroborate 4-Toluenediazonium triiodide
Azocarbaboranes 1,1-‘Azo-1,2-dicarbadecaborane	**Aziridines** 1-Bromoaziridine
N-Azolium nitroimidates Benzimidazolium 1-nitroimidate 4-Nitroamino-1,2,4-triazole	**Isoxazoles** 3-Aminoisoxazole 3,5-Dimethylisoxazole
Triazoles 3-Diazo-5-phenyl-3H-1,2,4-triazole 4-Hydroxy-3,5-dimethyl-1,2,4-triazole 1,2,3-Triazole	**Tetrazoles** 5-Aminotetrazole Silver and mercury salts of 5-nitrotetrazole Tetrazole
Alkyl perchlorates Hexyl perchlorate Ethyl perchlorate 1-Chloro-2-propyl perchlorate	**Acyl hypohalites** Acetyl hypobromite Hexafluoroglutaryl dihypochlorite
Iodine Compounds Calcium 2-iodylbenzoate Iodobenzene 2-Iodylvinyl chloride	**Difluoroaminoalkanols** 1,1-Difluorourea Perfluoro-N-cyanodiaminomethane
Fluoro—nitro compounds 1-Fluoro-1,1-dinitrobutane Fluorodinitromethyl azide	**Perchloryl Compounds** 2,6-Dinitro-4-perchlorylphenol Perchloryl fluoride N-Perchloryl piperidine

Alkyl nitrates Ethylidene dinitrate Glyceryl trinitrate Propyl nitrate	**Aromatic nitrates** Picric acid Trinitrobenzene Picryl sulfonic acid Trinitroresorcinol
Nitroaryl Compounds N-Chloro-4-nitroaniline	**Nitroso Compounds** Dinitrosylnickel Ethyl N-methyl-N-nitrosocarbamate Potassium nitrosodisulfate
Polynitroaryl Compounds 5,6-Dinitro-2-dimethyl aminopyrimidinone 4-Nitro-1-picryl-1,2,3-triazole 2,4,6-Trinitrotoluene	**Polynitroalkyl Compounds** Dinitroacetonitrile Hexanitroethane Potassium trinitromethanide
Nitrogenous Base Nitrite Salts Methylammonium nitrite	**Furazan N-oxides** Dicyanofurazan N-oxide 4-Oximino4,5,6,7-tetrahydrobenzofurazn N-oxide
aci-Nitroquinonoid Compounds Sodium 1,4-bis(aci-nitro)-2,5-cyclohexadienide	**Picrates** Nickel picrate (anhydrous) S-7-Methylnonylthiouronium picrate Sodium picrate
aci-Nitro Salts Ammonium aci-nitromethanide Dipotassium aci-dinitromethanide Thallium aci-phenylnitromethanide	**Amminemetal oxosalts** Ammonium hexanitrocobaltate Bis(1,2-diaminoethane) diaquacobalt (III) perchlorate Trihydrazine nickel (II) nitrate
Allyl trifluoromethanesulfonates 2-Chloro-2-propenyl trifluoromethanesulfonate	**Acetylene or acetylide compounds:** N-Chloro-3-aminopropyne Propiolic acid Propynethiol
Strained-Ring Compounds 2-Azatricyclo[2.2.102,6]hept-7-yl perchlorate Dicyclopropyldiazomethane Prismane	**N-Metal Derivatives** Cadmium nitride Dibutylthallium isocyanate Sodium amide
Fulminating metals Lead fulminate Gold fulminate Silver fulminate	**Metal Fulminates** Mercury (II) fulminate Sodium fulminate Tripropyllead fulminate
Perchloramide Salts Barium perchloramide Mercury (II) N-perchloryl benzylamide Silver perchlorylamide	**Metal Nitrophenoxides** Lithium 4-nitrothiophenoxide Potassium 4-nitrophenoxide
Metal Halogenates Lead bromate	**Metal Hydrides** Stibine (Antimony hydride)
Metal Oxometallates Bis (benzene) chromium dichromate	**Metal Oxohalogenates** Ammonium iodate Lead acetate–lead bromate

Metal Perchlorates Chromyl perchlorate	**Metal Picramates** Palladium picramate Uranyl picramate
Metal Peroxides Many transition metal peroxides are dangerously explosive.	**Silver Compounds** Silver nitride (fulminating silver) Disilver ketenide Phenylsilver Silver azide Silver Osmate
Metal Peroxomolybdates 2-Potassium tetraperoxomolybdate 2-Sodium tetraperoxomolybdate	**Hydroxooxodiperoxochromate salts** 1-Ammonium hydroxooxodiperoxochromate Potassium hydroxooxodiperoxochromate
Peroxyacid salts Calcium peroxodisulfate Potassium tetraperoxomolybdate Tetramethylammonium pentaperoxodichromate	**Peroxy and Iodoxy acids** Benzenperoxyselennic acid Peroxyacetic acid Peroxyformic acid o-Iodoxybenzoic acid (IBX)
Peroxycarbonate esters O-O-tert-Butyl isopropyl monoperoxycarbonate Diallyl peroxydicarbonate Dimethyl peroxydicarbonate	**Phosphorus esters** Diethyl phosphite Dibenzyl phosphorchloridate
Oximes Bromoacetone oxime Hydroxycopper glyoximate Potassium cyclohexanehexone 1,3,5-trioximate	**N–S Compounds** Disulfur dinitride Potassium sulfurdiimidate Tetrasulfur tetranitride Thiotrithiazyl nitrate
Oxosalts of **Nitrogenous Bases** Ammonium tetranitroplatinate (II) Diamminepalladium (II) nitrate 1,2-Diammonioethane nitrate	**Organolithium Reagents** o-Trifluoromethyl phenyllithium m-Bromo phenyllithium
Ozonides trans-2-Butene ozonide Ethylene ozonide (1,2,4-trioxolane) Trifluoroethylene ozonide	**Organomineral Peroxides** Bis(triethyltin) peroxide Diethylhydroxotin hydroperoxide
Perchlorate Salts of Nitrogenous Bases Pyridinium perchlorate Teteraethylammonium perchlorate	**Poly(dimercuryimmonium) Compounds** Poly(dimercuryimmonium picrate) Poly(dimercuryimmonium permanganate) Poly(dimercuryimmonium trinitrobenzoate)
Polymerisation (violent) Acrylic acid Ethylene oxide Vinyl acetate	

Appendix II Chemicals that May Explode due to Over-pressurised Containers

Note this is not an exhaustive list, please consult the SDS.

Allyl chloroformate	Aluminum chloride	Aluminum lithium hydride
Ammonia solution	Ammonium hydroxide	Ammonium persulfate
Anisyl chloride	Aqua regia	Benzenesulfonyl chloride
Benzyl chloroformate	Bleach	Bleaching powder
Calcium carbide	Calcium hydride	Calcium hypochlorite
Chloroform	Chromic acid	Cumene hydroperoxide
Cyclohexene	Diethyl pyrocarbonate	Dimethylamine
Formic Acid	Hydrogen peroxide	Isopropyl chloroformate
Lauroyl peroxide	Lithium aluminum hydride	Lithium hydride
Nitric acid	Nitrosoguanidine	Peracetic acid
Phenol	Phosphorus trichloride	Potassium Persulfate
Silicon tetrachloride	Sodium borohydride	Sodium dithionite
Sodium hydride	Sodium hydrosulfite	Sodium hypochlorite
Sodium peroxide	Sodium persulfate	Thionyl chloride
Urea peroxide	Zinc	

References:

- BRÄSE, S., GIL, C., KNEPPER, K., ZIMMERMANN, V. “ORGANIC AZIDES: AN EXPLODING DIVERSITY OF A UNIQUE CLASS OF COMPOUNDS” ANGEW. CHEM. INT. ED., 2005, 44, 5188.
- KOLB, H.C., FINN, M.G., SHARPLESS, K.B., “CLICK CHEMISTRY: DIVERSE CHEMICAL FUNCTION FROM A FEW GOOD REACTIONS,” ANGEW. CHEM. INT. ED. 2001, 40, 2004-2021.
- TREITLER, D. S. LEUNG. HOW DANGEROUS IS TOO DANGEROUS? A PERSPECTIVE ON AZIDE CHEMISTRY. J. ORG. CHEM. 2022, 87, 11293−11295