UNIVERSITY OF VICTORIA
**Occupational Health, Safety and Environment**

**Chemical Safety – Special Hazards**

**Safe Work Procedure (SWP – 014)**

# Pyrophoric and Water Reactive Chemicals

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**REVISION HISTORY**

| | *Revision Date* | *Author* | *Position* |
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**DOCUMENT APPROVAL**

*Approved by*: Laboratory Safety Committee

| Jody Spence | December 4, 2023 |
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| *Chair, Laboratory Safety Committee* | *Date Approved* |

**This revision replaces all previous versions of this document. If a copy is printed, it is the users' responsibility to verify the copy is the most current version of the document.*

University of Victoria

## PURPOSE

To provide guidance and instruction of the safe handling and use of liquid or solid pyrophoric and/or water reactive chemicals in laboratories. In addition to this general Safe Work Procedure (SWP), each lab must develop a lab-specific work procedure unique to the experiments and activities being performed. The Lab SWP must be reviewed by OHSE (see Procedures, #7).

## SCOPE

This SWP covers the general use and safe handling of liquid or solid pyrophoric and/or water reactive chemicals in the liquid or solid state. Pyrophoric gases will not be covered in this SWP. Techniques how to handle or manipulate pyrophoric materials will be mentioned but the specific techniques will not be covered. Refer to "An illustrated Guide to Schlenk Line Techniques" cited in the reference 7 below to review Schlenk techniques and methods. It is the expectation that the Lab SWP will describe how to set up and perform the technique.

## TRAINING

The following training is required to be completed prior to working with pyrophoric and/or water reactive chemicals:

- WHMIS
- Lab Safety for Lab Workers
- Lab SWP with documented signoff by the individual and their supervisor.

Refresher training in the General and Lab SWP must be provided when:

- There has been an extended absence or
- There has been an incident or injury, or
- 2 years has elapsed since the original training.

## REGULATION AND POLICY

The University of Victoria will follow WorkSafeBC Occupational Health and Safety Regulation Part 5 and 30 and the University of Victoria Occupational Health, Safety & Environment Department.

## RESPONSIBILITY

It is the responsibility of personnel undertaking activities with special hazards to complete all required training and adhere to these safe work procedures, including any additional lab or job-specific procedures.

It is the PI's or supervisor's responsibility to ensure that individuals working with special hazards have been trained prior to commencing work and have demonstrated competency in safely performing all duties associated with the special hazard in accordance with these procedures.

## DEFINITIONS

PPE – Personal protective equipment
Schlenk techniques – glassware and methods to handle materials under inert atmosphere
Quench – The process of deactivating a reactive chemical and making a less reactive product for safe handling and/or disposal

## MATERIALS

A sand bucket should be readily accessible should an accidental fire occur. Class A or B fire extinguishers are ineffective against fires from these chemicals. Class C fire extinguishers work for certain pyrophorics but not any metal containing materials; hence, consider a Class D fire extinguisher or sand. A glove box or Schlenk line and Schlenk glassware are necessary to handle and manipulate the majority of pyrophoric and/or water reactive chemicals.

## HAZARD

Pyrophoric chemicals are defined as chemicals that react with air (oxygen) and ignite within seconds or minutes. Whereas water reactive chemicals are those chemicals which ignite due to moisture in the air or in contact with water. Many chemicals can be either pyrophoric or water reactive or both; nevertheless, the hazards and risks associated with both pyrophoric and water reactive chemicals in either solid or liquid state are similar. Pyrophoric and/or water reactive solids or liquids are typically packaged in inert atmospheres, while solids are sometimes instead dispersed in mineral oil or other diluent. Pyrophoric and/or water reactive chemicals themselves are health hazards; in many cases their by-products from igniting in air or reaction of water are highly toxic. Always consult the SDS to understand the possible by-products and what precautions to take. Always plan ahead and be prepared with experiment setup before starting to work with pyrophorics and/or water reactive chemicals. Eliminate or substitute for a less hazardous material whenever possible.

Examples of pyrophoric and/or water reactive solids include but are not limited to:

- Finely divided metal powders (e.g. calcium, nickel, iron, magnesium, titanium, uranium, zirconium)
- Alkali metal (e.g. lithium, sodium, potassium)
- Low valent metal compounds (e.g. titanium dichloride)
- Non-metals (e.g. white phosphorous)
- Metal hydrides (e.g. potassium hydride, sodium hydride, lithium aluminum hydride, uranium trihydride)
- Non-metal hydrides (e.g. arsines, germanes, silanes)
- Organometallics (e.g. dimethylaluminum chloride, diethylethoxyaluminium, dicobalt octacarbonyl, tetrabenzyl titanium, trimethylanalum dichloride, nickel carbonyl)
- Hydrogenation catalysts (e.g. Raney Ni, are especially hazardous due to adsorbed hydrogen)
- Finely divided iron sulfides, potassium sulfide, aluminum phosphide

Examples of pyrophoric and/or water reactive liquids/solutions include but are not limited to:

- Alkali metals and organometallics (e.g., sodium potassium amalgam, sodium mercury amalgam, t-butyllithium, trimethylaluminum, and diethylzinc)
- Alkyl metal halides (e.g., diethylaluminum bromide, DIBAH)
- Alkyl magnesium halides ‘Grignard reagents’ (e.g., methylmagnesium bromide)
- Alkylphosphines (e.g., triethylphosphine)
- Boranes (e.g., borane dimethylsulfide complex)
- Low valent metal compounds (e.g. titanium tetrachloride)

## PROCEDURE

### 1. Handling

a. Review the SDS before attempting to handle pyrophorics.
b. Always wear PPE
    i. Wear eye protection
    ii. Wear a flame retardant lab coat
    iii. Wear nitrile gloves
    iv. Consider a flame retardant apron when handling larger volumes or quenching pyrophorics
c. Never work alone when handling pyrophoric and/or water reactive chemicals.
d. Avoid working with pyrophorics after hours or on weekends.
e. Use of a glovebox or a Schlenk line in a fume hood with inert gas flow will be necessary.
f. Use the least amount of material possible to achieve the desired result.
g. Do not exceed the scale of procedures without approval of the PI.
    i. Consider performing the reaction multiple times in small scale than to perform one larger scaled reaction.
h. Limit or remove any ignition sources near or in the fume hood.
i. Ensure dry sand and/or an appropriate fire extinguisher is kept nearby.
j. Transferring pyrophoric liquids on a Schlenk line:
    i. Use Luer lock syringes and long needles for small volumes (less than 20 mL)
    ii. Use the cannula method for large volumes (more than 20 mL)
    iii. Use a clamp or ring stand to secure containers of pyrophoric liquids during transfer.
k. Handling pyrophoric and/or water reactive solid blocks in dispersion outside of glovebox (e.g. sodium metal in oil):
    i. Cut pieces in the packing oil
    ii. Use forceps to transfer to beaker with toluene to wash off oil.
    iii. Use forceps to transfer again to weighed flask of toluene (if required).
    iv. Do not use low boiling solvent for washing oil, such as ether and pentane, as they tend to condense water upon evaporation.
l. Remove dispersant of pyrophoric and/or water reactive solid powders using Schlenk techniques (e.g. potassium hydride dispersed in mineral oil):
    i. Several methods or techniques are possible to remove the dispersant, choose one appropriate for the specific chemical.
    ii. Handle pyrophoric powders (such as sodium hydride) without dispersant in a glovebox.
m. Some water reactive chemicals (such as lithium aluminum hydride and sodium hydride) may be handled in the air for brief periods of time, but the containers must be flushed with inert gas or submerged in oil/dispersant before storage.
n. Crack open ampules only in a glovebox.
    i. Transfer ampules in a glovebox using a secondary container.

### 2. Storage

a. Store pyrophoric chemicals under an inert atmosphere (glove box, inert gas-filled desiccators or sealed glass containers) OR submerged in an inert liquid (e.g. oil for alkali metals, water for Raney metals).
b. Do not store with flammables or oxidizers.

c. Do not store in areas with heat/flames or water source.
d. Prevent containers of pyrophorics from leaking or breaking.
e. Store ampules of pyrophorics in a secondary container until they are needed.
f. Include date received on all containers.
g. Include date opened or first used on all containers

**3. Spills**

a. Follow OHSE's general spill response instructions
b. Do not attempt to clean up any spill if not trained or beyond your capability. Seek assistance or call Campus Security (250-721-7599)
c. Specific steps for small spills:
    i. Exert extreme caution due to potential spontaneous combustion and potential ignition of flammable solvents or other materials in the area
    ii. If smoke or fire is observed at any point while cleaning up spill, immediately vacate, warn others and call 911
    iii. Do not use paper towels to cover or contain the spill
    iv. Use dry sand to cover and smother the spill.
    v. Carefully quench by slow addition of isopropanol.
    vi. After complete quench, double bag spill residues for hazardous waste pickup.
b. Specific steps for small spills in a glove box
    i. Clean up spill with Kim wipes
    ii. Use toluene to wipe glove box surface
    iii. Collect Kim wipes in a vial or container
        - If planning to quench:
            a. Ensure contents are dissolved and/or submerged
            b. Add additional toluene if necessary and close vial or container
            c. Remove vial or container from glove box
            d. Open container and carefully quench by slow addition of cold isopropanol
            e. After complete quench, seal vial or container and submit for hazardous waste pick up.
        - If not planning to quench:
            a. Seal vial or container and tape shut
            b. Remove vial or container from glove box
            c. Double bag vial or container
            d. Submit for hazardous waste pick up
d. Specific steps for larger spills:
    i. Secure the area and warn others.
    ii. Immediately evacuate the spill area.
    iii. Posting "do not enter" signs on the doors of the lab.
    iv. Call 911 and Campus Security at 250-721-7599.
e. Complete a *Department Incident & Investigation Report* to document and review the spill incident.

## 4. Decontamination

a. Do not leave containers with residues of pyrophoric materials open to the atmosphere.
b. Rinse lab consumables (e.g. pipettes) with residual pyrophorics in the glove box into a sealed flask or vial
c. Collect any washings and kim-wipes used in the glove box contaminated with pyrophoric solid or liquid into a flask or vial to quench.
d. Quench residues as appropriate for the type of pyrophoric and/or water reactive chemical used. Typical quenching method is with toluene and isopropanol mixture, followed with addition of ethanol or methanol.
    i. Consider cooling the container with an ice bath or dry ice/acetone before quenching
e. Clean needles and cannulas immediately to prevent clogging of the needles and seizing the syringes.
f. If labware has a noxious odor, soak labware in bleach overnight before further cleaning or disposing.

## 5. First Aid and Emergencies

a. Call 911 to summon an ambulance if there is a medical emergency.
b. Call Campus Security at 250-721-7599 for first aid.
c. If a fire occurs, use an appropriate fire extinguisher or immediately exit the lab and warn others.
d. If anyone is exposed, or on fire, rinse with copious amounts of water at the nearest emergency shower.
e. Immediately report emergency to PI/supervisor and OHSE

## 6. Waste Disposal

a. Small amounts of unused or unwanted pyrophoric materials are recommended to be destroyed by careful quenching of the residue.
b. Review and plan accordingly the method and appropriate material to quench pyrophoric and/or water reactive chemicals (e.g. quenching hydrogenation catalysts do not follow the common method).
c. A common method of quenching pyrophoric and water reactive chemicals:
    i. Transfer the pyrophoric material to an appropriate reaction flask containing a stirbar.
    ii. Dilute significantly with a high boiling unreactive solvent such as toluene
    iii. Place the flask in an ice water bath
    iv. Slowly add isopropanol to quench pyrophoric material with vigorous stirring.
    v. Add additional isopropanol until there is no obvious reactivity
    vi. Slowly add methanol, a more reactive quenching agent.
    vii. Add additional methanol until there is no obvious reactivity
    viii. Add water dropwise to ensure there is no further reactivity
    ix. Dispose quenched solution as hazardous waste
d. If not quenching residue of unused and remaining pyrophoric and/or water reactive chemicals
    i. Ensure material is diluted with an inert liquid (such as toluene or mineral oil)
    ii. Container or vial is sealed and secured (e.g. use electrical tape to seal lid)
    iii. Affix a green hazardous waste sticker on the container and submit for hazardous waste disposal.

e. Do not quench large quantities of pyrophoric chemicals (e.g. old bottle of an unused Grignard reagent)

    i. Affix a green hazardous waste sticker on the bottle for hazardous waste disposal.

f. Dispose of any container that appears damaged or corroded as hazardous waste.

**7. Lab SWP**

In additional to this general SWP, each lab that is using pyrophoric and/or water reactive chemicals requires a Lab SWP that includes specific procedures for:

a. Details of the pyrophoric and/or water reactive chemicals
b. Details of dangerous by-products after exposure of pyrophoric and/or water reactive material to air or water/moisture.
c. Max scale permitted
d. Specific techniques used in handling pyrophoric and/or water reactive chemicals
e. List of materials to keep away from or close to the work space
f. Spill and emergency response
g. First aid measures

**REFERENCES**

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