Pyrophoric & Water-Reactive Chemicals- Safe Work Practices

Introduction

Pyrophoric liquids and solids spontaneously ignite within 5 minutes after coming into contact with air. Water-reactive chemicals become spontaneously flammable or emit flammable gases in potentially dangerous quantities upon contact with water, steam or moisture. The reactive nature of these chemicals makes proper training, handling, storage, and control measures critical to ensuring the health and safety of researchers. Failure to comply with safety measures can lead to fires, explosions, property damage and serious injuries or even death. This document provides guidelines for the safe use of pyrophoric and water-reactive chemicals in laboratories.

Hazards

The main hazard associated with pyrophoric and water-reactive chemicals is **fire** upon contact with air or moisture. The high level of **reactivity** associated with these chemicals requires them to be handled in inert atmospheres, free of ignition sources. The hazards associated with these chemicals is exacerbated by the fact that many are stored in highly flammable solvents (e.g., diethyl ether, hexane, pentane, tetrahydrofuran, etc.), further increasing the risk and severity of fires.

In addition to reactivity and flammability, many of these chemicals are also classified as acutely toxic, corrosive, reproductive toxins, peroxide-forming agents or capable of damaging the liver, kidneys, and central nervous system. **Safety data sheets (SDSs)** should indicate the hazards pertaining to specific pyrophoric or water-reactive chemicals being used in the lab. Strict adherence to standard operating procedures and safe work practices should be followed to ensure safe usage.

Common Pyrophoric & Water Reactive Chemicals

Below is a table of common pyrophoric and water-reactive chemicals found in laboratories. Be aware that particle size, moisture and the thermodynamics of metal oxide or metal nitride formation impacts the reactivity of many pyrophoric metals. This list is not comprehensive.

Pyrophoric & Water-Reactive Chemicals

Class	Examples
Alkali metal amides	Lithium amide
Grignard Reagents	RMgX (R=alkyl, X=halogen)
Halides of nonmetals	Silicon tetrachloride, boron trifluoride
Inorganic acid halides	Phosphorus oxychloride, thionyl chloride
Metal alkyls and aryls	Alkyl lithium compounds; tert-butyl lithium
Metal carbonyls	Lithium carbonyl, nickel tetracarbonyl
Metal powders (finely divided)	Cobalt, iron, zinc, zirconium
Metal hydrides	Sodium hydride, lithium aluminum hydride
Nonmetal hydrides	Diethylarsine, diethylphosphine
Non-metal alkyls	Tetramethyl silane, tributyl phosphine
Non-metallic elements	White and red phosphorus
Group I (Alkali) metals	Lithium, potassium, sodium, sodium-potassium alloy, rubidium, cesium, francium
Gases	Silane, dichlorosilane, diborane, phosphine, arsine

Safe Work Practices

Administrative/Work Practice Controls

- Safety training should be provided by the principal investigator or other qualified personnel to all researchers working with pyrophoric and/or water-reactive chemicals. Documented training is recommended.
- Read the **safety data sheet (SDS)** for each reactive chemical prior to use.
- Eliminate, substitute less toxic chemicals or reduce the quantities of pyrophoric or water-reactive chemicals being used if possible.
- Researchers should not work alone with pyrophoric or water-reactive chemicals.
- Experiments should be performed during normal business hours (i.e., 8:00am-5:00pm Monday- Friday) if possible.
- Argon is generally preferred over nitrogen as an inert gas because it is heavier than air.
- Multiple transfers of small volumes of pyrophoric liquids are preferred over a single transfer of larger quantities.

Engineering Controls

- Solid pyrophoric chemicals should be handled in an inert atmosphere glove box. In some cases, inert atmosphere glove bags can be used as an alternative.
- The glove box or fume hood where pyrophoric or water reactive chemicals will be used should be clear of all nonessential chemicals, combustible materials (e.g., paper towels, Kimwipes, etc.), and equipment.
- If a glove box or bag is not available, manipulation of these reagents via syringe or cannula should always be conducted in a certified chemical fume hood, over a spill tray if possible, with the sash at the lowest practicable working height.
- Needles should be equipped with locking mechanisms to prevent accidental disconnection and release of reagents.

- Mineral oil bubblers must be employed at all times to release excess pressure from reagent or reaction vessels that can contribute to accidents.
- Balloons used for air-sensitive reagents are **not** suitable with pyrophoric chemicals.
- Portable blast shields placed inside the fume hood can be used as a protection barrier.

Personal Protective Equipment

- At a minimum, chemical splash goggles or safety glasses that meet American National Standards Institute (**ANSI**) standard Z-87.1 must worn must be worn when handling pyrophoric or water reactive chemicals.
- Full face-shields may be required when the risk of splashes or highly exothermic reactions exists.
- Nitrile gloves should be adequate for handling small quantities. Heavy, chemical-resistant gloves, Nomex or related aramid fiber gloves may be more appropriate for working with large quantities.
- It is recommended that leather or Kevlar gloves be worn underneath nitrile gloves for fire protection purposes.
- A flame resistant lab coat should be worn when working with pyrophoric and water reactive chemicals. Lab coats should be buttoned and fit properly to cover as much skin as possible.
- Shirts, pants and other clothing worn in labs should be cotton or wool. Synthetic clothing is strongly discouraged in laboratories where pyrophoric chemicals are used.
- Closed-toed footwear, which covers the entire foot, must be worn when working with pyrophoric/water-reactive chemicals.

Storage

- Store reactive materials as recommended in safety data sheets (SDSs).
- Do not store reactive chemicals with flammable materials or in a flammable liquids storage cabinet.
- Pyrophoric liquids, or compounds dissolved in a liquid, should be stored in sealed containers with PTFE-lined septa to prevent air exposure.
- Ensure that sufficient protective solvent, oil, kerosene, or inert gas remains in the container while the material is stored.
- An inert gas-filled desiccator or glove box may be a suitable storage location for most materials.
- If pyrophoric or water reactive reagents are received in a specially designed shipping, storage or dispensing container, ensure that the integrity of that container is maintained.
- Never return excess chemical to the original container. Small amounts of impurities introduced into the container may cause a fire or explosion.

Eyewash/Safety Showers

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- An approved eyewash station and safety shower must be immediately available within 10 seconds for emergency use.
- Keep the area around shower and eyewash station clear of obstructions at all times.
- Always know the exact location of your eyewash and shower and how to use all emergency equipment.
- Test your eyewash weekly. Safety showers should be tested annually by Facilities & Operations.

Additional Resources

Occupational Safety & Health Administration- Appendix B to §1910.1200 - Physical Hazards

http://www.osha.gov/dsg/hazcom/hazcom-appendix-b.html

Yale Environmental Health & Safety- Pyrophoric Handling Policy

http://www.yale.edu/ehs/Documents/chem/pyrophoricpolicy.pdf

Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards

http://www.ehs.uconn.edu/Chemical/Prudent%20Practices%20in%20the%20Laboratory.pdf