

Safe Use of Pyrophoric/Water Reactive Materials

Introduction

Pyrophoric and water reactive materials can ignite spontaneously on contact with air, moisture in the air, or water. Improper handling of these materials can cause fire or explosion, resulting to serious injuries, death and/or significant damage to facilities.

The purpose of this job aid is to advise the campus community how to use, store, and dispose of pyrophoric/water reactive chemicals in a manner that will minimize risks to personnel, university facilities, and the environment. This applies to all laboratories – both clinical and research.

Examples of Pyrophoric/Water Reactive Materials

Grignard Reagents:	RMgX (R=alkyl, X=halogen)
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:	R ₃ B, R ₃ P, R ₃ As; tetramethyl silane, tributyl phosphine
White and red phosphorus	
Group I (Alkali) metals:	Lithium, potassium, sodium, sodium-potassium alloy (NaK), rubidium, cesium, francium
Gases:	Silane, dichlorosilane, diborane, phosphine, arsine

Controlling the Hazards

Here is a list of things you should remember and do when working with or around pyrophoric/water reactive materials.

- Obtain all of the training in proper lab technique and be able to demonstrate proficiency if you use reactive materials.

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- Read Safety Data Sheets (SDS), SOPS, and guidance documents to understand how to control the hazards **BEFORE** starting work.
- Never work alone!
- **ALWAYS wear the appropriate personal protective equipment (PPE)!**
 - This includes:
 - 100% cotton or fire resistant lab coats,
 - safety goggles/face shield, and
 - appropriate hand protection.
 - If the reactive material were to ignite and spill onto the hand, nitrile or latex gloves would also ignite and contribute to serious injury.
 - Nomex and related aramid fiber products are excellent fire retardant materials.
 - Always wear street clothes and underwear made from cotton for better protection.
- Remove all excess and nonessential chemicals and equipment from the fume hood or glove box where pyrophoric or water reactive chemicals will be used.
- Keep combustible materials, including paper towels, away from reactive reagents.
- Keep the amount of pyrophoric or water reactive material present in your lab to the smallest amount practical.
- Use and handle the smallest quantity practical.
 - It is better to do multiple transfers of small volumes than attempt to handle larger quantities (greater than about 20 mL).

Emergency Equipment

Researchers working with reactive materials must have the proper equipment and the emergency phone numbers readily available for any emergencies, prior to starting the experiment.

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- Make sure there are enough quantities of acceptable extinguishing media like soda ash (lime) or dry sand to respond to fires.
- **DO NOT use water** to extinguish a pyrophoric/reactive material fire as it can actually enhance the combustion of some of these materials, e.g. metal compounds.
- Ensure that the eyewash/safety shower is within 10 seconds travel time and accessible through only one door.
- Perform all manipulations in an approved chemical fume hood or a glove box.

Storage

- Store reactive materials as recommended in the SDS.
- Use and store minimal amounts of reactive chemicals in the area.
- **Do not store reactive chemicals with flammable materials or in a flammable liquids storage cabinet.**
- Clear label containers carrying reactive materials with:
 - the correct chemical name,
 - in English, and
 - the appropriate hazard warning.
- Ensure that the integrity of that container is maintained if the pyrophoric or water reactive reagents are received in a specially designed shipping, storage, or dispensing container (such as the Aldrich Sure/Seal packaging system).
- Check to see if sufficient protective solvent, oil, kerosene, or inert gas remains in the container while the material is stored.
- **NEVER** return excess chemical to the original container. Small amounts of impurities introduced into the container may cause a fire or explosion.

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Disposal of Pyrophoric Reagents

- Never leave any container with a residue of reactive materials open to the atmosphere.
- Destroy any unused or unwanted reactive materials by transferring the materials to an appropriate reaction flask for hydrolysis and/or neutralization with adequate cooling.
 - Rinse the empty container three times with an inert dry COMPATIBLE solvent
 - Ensure that the rinse solvent is also neutralized or hydrolyzed.
 - Add and remove the rinse solvent from the container under an inert atmosphere.
- Leave the container open in back of a hood or ambient atmosphere at a safe location for at least a week - after the container is triple-rinsed.
- Dispose of all materials – disposable gloves, wipes, bench paper, etc. - that are contaminated with pyrophoric chemicals as hazardous waste.
 - Properly contain contaminated waste that must be left overnight in the open laboratory in order to prevent fires.

Standard Operating Procedure (SOP) Requirement

- Laboratories working with pyrophorics/water reactives must develop lab specific Standard Operating Procedures (SOPs) and must provide training to the users of these materials.
- Users must read and understand the SOP and any other reference material available to them.

Handling Pyrophoric Liquids

By using proper syringe techniques, these reagents can be handled safely in the laboratory. The Aldrich Sure/Sea Packaging System provides a convenient method for storing and dispensing air-

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sensitive reagents. Dispense the reagent using a syringe or double-tipped needle (cannula) (16, 18 or 20 gauge) inserted through the hole in the metal cap.

Emergency Procedures

Spills

- **DO NOT use water** to extinguish a reactive material fire as it can actually enhance the combustion of some reactive materials, e.g. metal compounds.
- Do not use combustible materials (paper towels) to clean up a spill, as these may increase the risk of igniting the reactive compound.
 - Use soda ash (powdered lime) or dry sand to completely smother and cover any small spill that occurs.
 - Keep a container of soda ash (powdered lime) or dry sand within arm's reach when working with a reactive material.
- If anyone is exposed, or on fire, wash with copious amounts of water, except if metal compounds are involved, which can react violently with water.
 - Smother the fire, if it is a metal fire. This is a better course of action.
- The recommended fire extinguisher is a standard dry powder (ABC) type.
 - Class D extinguishers are recommended for combustible solid metal fires (e.g., sodium, LAH), but not for organolithium reagents.
- Call 9-1-1 for emergency assistance and for assistance with all fires, even if extinguished.