

Safety Net #135

Procedures for Safe Use of Pyrophoric/Water Reactive Reagents

Introduction

Pyrophoric and water reactive materials can ignite spontaneously on contact with air, moisture in the air, oxygen, or water. Failure to follow proper handling procedures can result in fire or explosion, leading to serious injuries, death and/or significant damage to facilities. This SafetyNet describes the hazards, proper handling, disposal and emergency procedures for working with pyrophoric and water reactive materials.

Any handling of a pyrophor/water reactive material is high risk and must be controlled with adequate system design, direct supervision and training. These tasks are two person tasks and workers should not work alone.

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_3B , R_3P , R_3As ; 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

Hazards

Because these reagents ignite on contact with air and/or water, they must be handled under an inert atmosphere and in such a way that rigorously excludes air/moisture. Some are toxic and many come dissolved or immersed in a flammable solvent. Other common hazards include corrosivity, teratogenicity, water reactivity, or peroxide formation, and may damage to the liver, kidneys, and central nervous system.

Controlling the Hazards

BEFORE working with pyrophoric or water reactive reagents, read the relevant Material Safety Data Sheets (MSDS), technical bulletins, and guidance documents to understand how to mitigate the hazards. The MSDS must be reviewed before using an unfamiliar chemical and periodically as a reminder. Users of reactive materials must be trained in proper lab technique and be able to demonstrate proficiency. Do not work alone or during off hours, when there are few people around to help. ALWAYS wear the appropriate personal protective equipment.

Remove all excess and nonessential chemicals and equipment from the fume hood or glove box where pyrophoric or water reactive chemicals will be used. This will minimize the risk if a fire should occur. Keep combustible materials, including paper towels and Kimwipes, 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). Alternatively, an appropriately engineered system, capable of safely handling the larger quantity must be designed, tested and properly used.

Personal Protective Equipment (PPE)

Eye Protection

- A full face shield that meet the ANSI Z.87.1 1989 standard must be worn whenever handling pyrophoric chemicals. Prescription eye glasses, safety glasses, and splash goggles will NOT provide adequate protection. A face shield, worn over safety eyewear, is required any time there is a risk of explosion, splash hazard or a highly exothermic reaction.
- All manipulations of pyrophoric chemicals which pose these risks must be carried out in a fume hood with the sash in the lowest feasible position.

Skin Protection

- In general, chemical protective gloves are unacceptable when working with pyrophors. 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, but can significantly reduce dexterity. A Nomex flight glove (used by pilots to protect from heat and flash) works well. Review the MSDS and contact EH&S for advice on appropriate gloves.
- ***A fire retardant lab coat must be worn.*** Special fire-resistant lab coats made from Nomex or other fire resistant materials are more expensive, but recommended for labs using these reagents routinely. Lab coats need to be buttoned and fit properly to cover as much skin as possible. Clothing, shirt and pants, should be cotton or wool. **Synthetic clothing is strongly discouraged.**
- Appropriate shoes that cover the entire foot (closed toe, closed heel, no holes in the top) must be worn.

Safety Equipment

Researchers working with reactive materials must have the proper equipment and the emergency phone number (9-1-1) readily available for any emergencies, prior to starting research activities. Acceptable extinguishing media include soda ash (lime) or *dry* sand to respond to fires. DO NOT use water to attempt to extinguish a pyrophoric/reactive material fire as it can actually enhance the combustion of some of these materials, e.g. metal compounds. A small beaker of dry sand or soda ash (lime) in the work area is useful to extinguish any small fire that occurs at the syringe tip and to receive any last drops of reagent from the syringe. Review the MSDS for the proper fire extinguisher to use with the given material.

Eyewash/ Safety Shower

- A combination eyewash/safety shower should be within 10 seconds travel time where reactive chemicals are used. Inside the laboratory is optimum.
- If a combination eyewash/safety shower is not available within the lab, an eyewash must be available (within 10 seconds travel distance) for immediate emergency use within the lab. Bottle type eyewash stations are not acceptable. A combination eyewash/shower must be available in the hallway or similar, within 10 seconds travel distance and accessible through only one door.

- Ensure that lab personnel know the locations of eyewashes and safety showers and the most direct route to access them.

Fume Hood

- Many reactive chemicals release noxious or flammable gases upon decomposition and should be handled in a laboratory hood. In addition, some pyrophoric materials are stored under kerosene (or other flammable solvent), therefore the use of a fume hood (or glove box) is required to prevent the release of flammable vapors into the laboratory.

Glove (dry) box

- Inert atmosphere glove boxes are an excellent device for the safe handling of reactive materials. Glove boxes used for this purpose should be in good working order and the moisture and oxygen levels of the atmosphere should be confirmed prior to introduction of reactive compounds into the box. Continuous monitoring of oxygen and moisture is highly recommended. Also, take into account interactions between items in the glovebox (e.g., nitrogen is not an inert gas for lithium metal as the lithium is reduced violently to lithium nitride).

Gas Cabinets

- Storage of pyrophoric gases is described in the California Fire Code, Chapter 41. Gas cabinets, with appropriate remote sensors and fire suppression equipment, are required.
- Gas flow, purge and exhaust systems should have redundant controls to prevent pyrophoric gas from igniting or exploding.
- Emergency back-up power should be provided for all electrical controls, alarms and safeguards associated with the pyrophoric gas storage and process systems.

Storage and Disposal

Storage

- Use and store minimal amounts of reactive chemicals. Do not store reactive chemicals with flammable materials or in a flammable liquids storage cabinet. Containers carrying reactive materials must be clearly labeled with the correct chemical name, in English, and hazard warning.
- Store reactive materials as recommended in the MSDS. An inert gas-filled desiccator or glove box are suitable storage locations for most materials.
- If pyrophoric or water reactive reagents are received in a specially designed shipping, storage or dispensing container (such as the Aldrich Sure/Seal packaging system) ensure that the integrity of that container is maintained.
- Ensure that 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.
- For storage of excess chemical, prepare a storage vessel in the following manner:
 - Dry any new empty containers thoroughly
 - Insert the septum into the neck in a way that prevents atmosphere from entering the clean dry (or reagent filled) flask.
 - Insert a needle to vent the flask and quickly inject inert gas through a second needle to maintain a blanket of dry inert gas above the reactive reagent.

- Once the vessel is fully purged with inert gas, remove the vent needle then the gas line. To introduce the excess chemical, use the procedure described in the handling section, below.

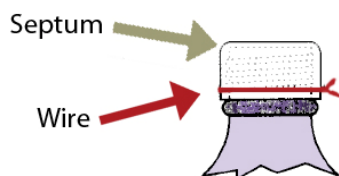


Fig. 1A Septum wired to vessel before accessing the reagent through the primary septum.

- For long-term storage, the septum should be secured with a copper wire (figure 1A).
- For extra protection a second same-sized septa (sans holes) can be placed over the first (figure 1b).
- Use parafilm around the outer septa and remove the parafilm and outer septum

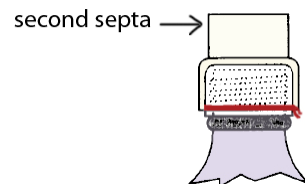


Fig. 1B For long-term storage, use a second septum

Disposal of Pyrophoric Reagents

- Any container with a residue of reactive materials should never be left open to the atmosphere.
- Any unused or unwanted reactive materials must be destroyed by transferring the materials to an appropriate reaction flask for hydrolysis and/or neutralization with adequate cooling.
- The empty container should be rinsed three times with an inert dry COMPATIBLE solvent; this rinse solvent must also be neutralized or hydrolyzed. The rinse solvent must be added to and removed from the container under an inert atmosphere.
- After the container is triple-rinsed, it should be left open in back of a hood or ambient atmosphere at a safe location for at least a week.
- The empty container, solvent rinses and water rinse should be disposed as hazardous waste and should not be mixed with incompatible waste streams.

Disposal of Pyrophoric or Water Reactive Contaminated Materials

- All materials – disposable gloves, wipers, bench paper, etc. - that are contaminated with pyrophoric chemicals should be disposed as hazardous waste. Proper and complete hazardous waste labeling of containers is vital. See SafetyNet #110 for more information on labeling hazardous wastes.
- The contaminated waste should not be left overnight in the open laboratory but must be properly contained to prevent fires.

Important Steps to Follow

Reactive reagents can be handled and stored safely as long as all exposure to atmospheric oxygen and moisture or other incompatible chemicals is avoided. Finely divided solids must be transferred under an inert atmosphere in a glove box. Liquids may be safely transferred without the use of a glove box by employing techniques and equipment discussed in the Aldrich Technical Information Bulletin AL-134. Pyrophoric gases must be handled in compliance with the California Fire Code, Chapter 41. Another good reference is “Manipulation of Air-sensitive Compounds” by Shriver and Drezdron.

The California Fire Code prohibits the storage or use of pyrophorics in buildings not fully protected by an automatic sprinkler system. If you are using a pyrophoric in an unsprinklered building contact the Fire Department at 2-1236 or EH&S at 2-1493 immediately so that we may assist you with the options available to mitigate the situation.

Handling Pyrophoric Liquids

- Users should read and understand the Aldrich Technical Information Bulletin No. AL-134. The PI should also have in place laboratory-specific handling, storage, and disposal standard operating procedures. The standard operating procedures should be included in the lab Chemical Hygiene Plan.
- By using proper syringe techniques, these reagents can be handled safely in the laboratory. The Aldrich Sure/Seal™ Packaging System provides a convenient method for storing and dispensing air-sensitive reagents. Schlenk glassware is another suitable option.
- The reagent can be dispensed using a syringe or double-tipped needle (canula) (16, 18 or 20 gauge) inserted through the hole in the metal cap, as shown in fig. 2 below. It is recommended that the plastic cap be replaced after each use and in particular for long-term storage.

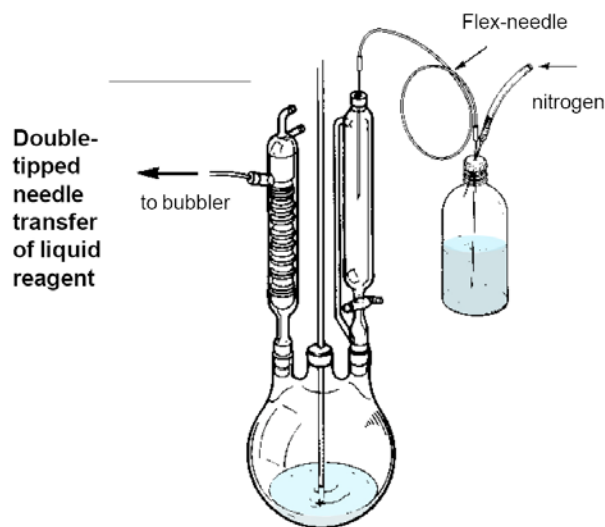


Fig. 2 Double-tipped needle transfer of liquid reagent

- For extended storage of unused reagents, use the solid plastic cap, or equip the bottle with an Oxford Sure/Seal valve cap, or transfer the reagent to a suitable storage vessel, as described above.

Emergency Procedures

Spill

- DO NOT use water to attempt 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. Soda ash (powdered lime) or dry sand should be used to completely smother and cover any small spill that occurs.
- A container of soda ash (powdered lime) or dry sand should be kept within arm's length 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. In the case of a metal fire, smothering the fire 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. Contact the Fire Department and review the MSDS for the appropriate fire extinguisher.

- Call 9-1-1 for emergency assistance and for assistance with all fires, even if extinguished.
- Pyrophoric gas releases and associated fires, should be extinguished by remotely stopping the gas flow. NEVER ATTEMPT TO PUT OUT A GAS FIRE IF THE GAS IS FLOWING.

Sources and Acknowledgements:

Created from a variety of sources including: Brandeis University, Standard Operating Procedure for Pyrophoric Chemicals; University of Nebraska, Lincoln, Pyrophoric Chemicals Standard Operating Procedure; University of Pittsburgh Safety Manual, Flammable and Pyrophoric Gas; Rochester University, SOP for Pyrophoric Chemicals. Images from Sigma-Aldrich Technical Bulletins [AL-134](#) and [AL-164](#).

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