

Procedures for Safe Use of Pyrophoric/Water-Reactive Reagents

A. Summary

Pyrophoric and water-reactive materials can ignite spontaneously or react violently 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.

Handling of pyrophoric/water-reactive materials are typically high-risk activities and must be controlled with adequate system design, direct supervision, and training. Never work alone with pyrophoric or water-reactive materials. At least one additional person trained in handling pyrophoric/water-reactive materials must be within visual range and capable of providing immediate assistance during the process.

NOTE: This guidance describes the hazards, proper handling, disposal, and emergency procedures for working with pyrophoric and/or water-reactive material. Labs handling pyrophoric and/or water-reactive material are required to have a standard operating procedure (SOP) in place.

B. Examples of Pyrophoric/Water-Reactive Materials

- Grignard Reagents: RMgX (R=alkyl, X=halogen)
- Metal alkyls and aryls: Alkyl lithium compounds, e.g., tert-butyl lithium
- Metal carbonyls: Lithium carbonyl, nickel tetracarbonyl
- Metal powders (finely divided): Cobalt, iron, zinc, zirconium
- Metal hydrides: Sodium hydride, lithium aluminum hydride
- Non-metal 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)
- Gases: Silane, dichlorosilane, diborane, phosphine, arsine

Pyrophoric and water-reactive materials can be identified using the Globally Harmonized System. Pyrophoric materials have the Hazard Code H250 (Catches fire spontaneously if exposed to air), while water-reactive materials have the Hazard Codes H260 (In contact with water releases flammable gases which may ignite spontaneously) and/or H261 (In contact with water releases flammable gas).

Please note, there are no GHS Hazard Codes that provide a means to readily identify water-reactive materials that produce a toxic gas as a secondary product.

C. Hazards

Because these chemicals may ignite/react violently 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. Many of

these materials come dissolved or immersed in a flammable solvent or oil. Gases commonly used for inert atmosphere reactions include nitrogen (N₂), argon (Ar), and helium (He). Argon and nitrogen are the most frequently used inert gases in laboratory settings due to their availability and suitable properties. For reactions involving highly reactive metals such as lithium, argon or helium are recommended due to their extreme inertness. The density of argon is greater than that of air and hence provides a better protection layer for inert atmosphere reactions.

Other common hazards of pyrophoric and water-reactive reagents may include corrosivity, teratogenicity, peroxide formation, and acute or chronic toxicity (may cause damage to the liver, kidneys, and central nervous system). All users should consult the relevant SOPs and applicable safety data sheets (SDSs) for guidance on how to address additional hazards.

D. Controlling the Hazards

- BEFORE working with pyrophoric or water-reactive reagents, read the relevant SDSs, technical bulletins, and guidance documents to understand how to mitigate the risks. The SDS must be reviewed before using an unfamiliar chemical and periodically as a reminder. Users of reactive materials must be trained in the laboratory-specific SOP(s) and be able to demonstrate proficiency. It is highly recommended that all users of pyrophoric/water-reactive materials complete hands-on fire extinguisher training.
- Never work alone or during off hours when there are few people around to help. At least one additional person trained in handling pyrophoric/water-reactive material must be within visual range, ready to provide emergency assistance if needed. ALWAYS wear the appropriate personal protective equipment (PPE).
- Remove all excess and nonessential chemicals and equipment from the fume hood or glove box where pyrophoric/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.
- Ensure that the appropriate quenching materials are prepared and at hand before any work with the pyrophoric/water-reactive material begins. Ensure that the appropriate extinguishing agent (i.e., dry sand, Met-L-X, soda ash, or lime) is within arm's reach during any work with pyrophoric/water-reactive materials. The appropriate quenching materials and extinguishing agents must be defined in the SOP prior to starting work.
- Keep the amount of pyrophoric/water-reactive material present in your laboratory 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 10 mL). Alternatively, an appropriately engineered system capable of safely handling the larger quantity must be designed, tested, and properly used (e.g., cannula transfer). More details on transfer techniques are available for reference.

E. Safety Equipment

Researchers working with reactive materials must have the proper safety equipment prior to starting research activities. Researchers must also have an emergency protocol in place (call 9-1-1 or activate other emergency communications).

Fire Extinguishers

- Acceptable extinguishing media, such as dry sand, Met-L-X, soda ash, or lime must be kept within arm's reach of the work area to respond to fires. DO NOT use water, carbon dioxide or Halon fire extinguishers to attempt to extinguish a pyrophoric/water-reactive material fire as they can actually enhance the combustion of some of these materials (e.g., metal compounds). A small beaker of dry sand, Met-L-X, soda ash, or lime in the work area is also useful to extinguish any small fire that occurs at the syringe tip and to receive any last drops of reagent from the syringe. Keep a Type D fire extinguisher in close proximity when working with combustible metals. An ABC fire extinguisher may be helpful to manage a collateral fire.

Eyewash/ Safety Shower

- A combination eyewash/safety shower should be available inside the laboratory, and within 10 seconds travel time where reactive chemicals are used.
- If a combination eyewash/safety shower is not available within the laboratory, an eyewash must be available (within 10 seconds travel distance) for immediate emergency use within the laboratory. 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 laboratory personnel know the locations of eyewashes and safety showers and the most direct route to access them.

Ventilation

- Inert atmosphere glove boxes are an excellent device for safe handling of pyrophoric/water-reactive materials. Glove boxes used for this purpose should be in good working order. The moisture and oxygen levels of the atmosphere should be confirmed prior to introduction of reactive compounds into the glove box. Continuous monitoring of oxygen and moisture is highly recommended. Potential interactions between items in the glove box should also be considered (e.g., nitrogen is not an inert gas for lithium metal as lithium is reduced violently to lithium nitride).
- If work in a glove box is not possible, all manipulation of pyrophoric/water-reactive materials must occur in a properly-functioning, certified chemical fume hood. Many pyrophoric/water-reactive chemicals release noxious or flammable gases upon decomposition. In addition, some pyrophoric/water-reactive materials are stored under kerosene (or other flammable solvents), therefore the use of a fume hood (or glove box) is required to prevent the release of flammable vapors into the laboratory.

Gas Cabinets

- Gas cabinets, with appropriate remote sensors and fire suppression equipment, are required.
- Gas flow, purge, and exhaust systems shall have redundant controls to prevent pyrophoric gas from igniting or exploding.
- Emergency back-up power shall be provided for all electrical controls, alarms, and safeguards associated with the pyrophoric gas storage and process systems.
- Additional info is available in the California Fire Code (2016 Edition), Chapter 64.

F. Safe Handling Procedures

Pyrophoric/water-reactive materials can be handled and stored safely as long as all exposure to atmospheric oxygen and moisture or other incompatible chemicals are 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, and described in detail herein. Pyrophoric gases must be handled in compliance with the California Fire Code, Chapter 64. Other good references include the following:

- How to Handle Pyrophoric Reagents, University of California, San Diego, [Working with pyrophoric reagents Eps 1: getting ready](https://www.youtube.com/watch?v=3_cBVfYVAC8) [https://www.youtube.com/watch?v=3_cBVfYVAC8](https://www.youtube.com/watch?v=WUHzcEunNY), [Transferring Pyrophoric Liquids Eps 2](https://www.youtube.com/watch?v=WUHzcEunNY) <https://www.youtube.com/watch?v=WUHzcEunNY>
- Lab Safety Academy: Pyrophorics, Dow Chemicals, [Lab Safety Academy: Pyrophorics](https://www.youtube.com/watch?v=mV189LDd7MM) <https://www.youtube.com/watch?v=mV189LDd7MM>
- 1. [Mikhail, A., et al., 2011. Methods for the safe storage; handling; and disposal of pyrophoric liquids and solids in the laboratory. Journal of Chem. Health & Safety, Vol. 18 \(Issue 1\), pp 5-10. ISSN 1871-5532, https://pubs.acs.org/doi/10.1016/j.jchas.2010.03.001.](https://pubs.acs.org/doi/10.1016/j.jchas.2010.03.001)

While these documents and videos provide an overview of the handling techniques, users must be trained on the laboratory's SOP and demonstrate competency in transfer techniques prior to handling pyrophoric/water-reactive materials.

- Users must read, understand, and follow manufacturer's recommendations and the required SOPs. The SOP must define laboratory-specific procedures for handling, storage, and disposal of pyrophoric/water-reactive material.
- By using proper syringe techniques, these reagents can be handled safely in the laboratory. The [Millipore Sigma Sure/Seal™ Packaging System](https://www.sigmaaldrich.com/US/en/technical-documents/technical-article/chemistry-and-synthesis/organic-reaction-toolbox/sureseal?srsId=AfmBOooNS_FDqX90uPAgwFR4JNaGv5G_jQSVz4oKIOYgoaKNATxw9zvp) https://www.sigmaaldrich.com/US/en/technical-documents/technical-article/chemistry-and-synthesis/organic-reaction-toolbox/sureseal?srsId=AfmBOooNS_FDqX90uPAgwFR4JNaGv5G_jQSVz4oKIOYgoaKNATxw9zvp and [ThermoFisher AcroSeal™ System](https://www.thermofisher.com/ie/en/home/chemicals/applications/acroseal-packaging.html) <https://www.thermofisher.com/ie/en/home/chemicals/applications/acroseal-packaging.html> provide a convenient method for storing and dispensing air-sensitive reagents.
- Many of these reagents are stored at reduced temperature. Before beginning any transfer, let the reagent bottle warm to room temperature in the fume hood or glove box. Water vapor can condense on the needle surface which could initiate ignition. Be sure to wipe any moisture off the bottle and septum.
- For guidance on proper technique for handling pyrophoric/water-reactive materials, see [Syringe and Cannula Techniques for Pyrophorics](https://www.csus.edu/college/natural-sciences-mathematics/internal/safety/_internal/_documents/pyrophoric-techniques-syringe-cannula-transfers.pdf) https://www.csus.edu/college/natural-sciences-mathematics/internal/safety/_internal/_documents/pyrophoric-techniques-syringe-cannula-transfers.pdf.

G. Storage and Disposal

Storage

- Pyrophoric and water-reactive chemicals must be properly segregated (i.e., not stored with other flammable materials) with secondary containment. Secondary containment that holds reactive materials must be clearly labeled with the correct chemical name, in English, and hazard warning.
- Reduced temperature storage of pyrophoric material requires a dedicated refrigerator approved for the storage of flammable materials.
- Store reactive materials as recommended in the SDS. An inert gas-filled desiccator or glove box are suitable storage locations for most materials.
- Use and store minimal amounts of pyrophoric/water-reactive chemicals.
- If pyrophoric or water-reactive reagents are received in a specially designed storage or dispensing container (such as the **Aldrich Sure/Seal™** or **ThermoFisher AcroSeal™** packaging system) ensure the integrity of the container is maintained.
- When applicable, ensure that sufficient inert gas, protective solvent/oil, or kerosene remains in the container while the material is stored.
- Only remove the desired quantity of pyrophoric/water-reactive reagent from the stock container. NEVER return excess reagent to the original container, as small amounts of impurities introduced into the container may cause a fire or explosion. Excess materials must be quenched according to the predetermined quenching scheme outlined in the SOP. Storage of any excess reagents outside of a glove box is discouraged. If necessary, storage vessels may be prepared in the following manner:
 1. Dry any new empty storage vessel thoroughly.
 2. The atmosphere inside the storage vessel must be composed of compatible inert gas.
 3. Insert a septum into the neck of the vessel in a way that prevents atmosphere from entering the clean and dry storage vessel. Ensure the storage vessel is sealed.
 4. Add the excess chemical into the storage vessel.
 5. For long-term storage, the septum should be secured with a copper wire (Figure 1A).
 6. For extra protection, a second same-sized septum (without holes) can be placed over the first (Figure 1B).

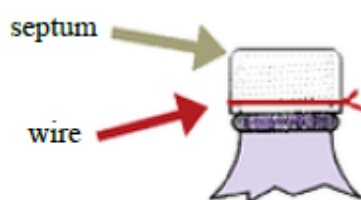


Figure 1A. Septum wired to vessel

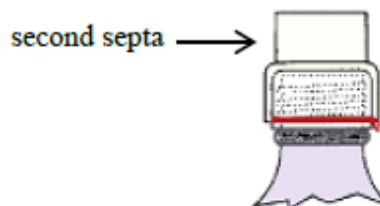


Figure 1B. For long-term storage, use a second septum

7. Parafilm around the outer septum may be used to prevent moisture from entering the storage vessel. For subsequent uses, remove the Parafilm and outer septum before accessing the reagent through the primary septum.

Disposal of Pyrophoric Reagents

- Any unused or unwanted reactive materials must be destroyed by transferring the materials to an appropriate reaction flask for quenching with adequate cooling. A quenching scheme for leftover reactive materials **must be developed BEFORE work begins** and defined in the appropriate pyrophorics or water-reactives SOP.
- The reaction flask should be rinsed three times with an inert, dry **compatible** solvent. The rinse solvent must be added to and removed from the container under an inert atmosphere. This rinse solvent must be neutralized or hydrolyzed before disposal using the method for quenching defined in the SOP.
- Any disposable or no longer needed reaction flasks and all solvent rinses used in the quenching process must be disposed of as hazardous waste and never 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 or water-reactive chemicals must be disposed as hazardous waste. Proper and complete hazardous waste labeling of containers is vital.

H. Personal Protective Equipment (PPE)

Eye Protection

- At a minimum, ANSI Z87.1-compliant safety glasses are required when working with air/water-reactive liquids. Indirectly-vented chemical splash goggles are required for processes where splashes are foreseeable or when generating aerosols. Prescription eyeglasses will NOT provide adequate protection.
- A face shield that meets ANSI Z.87.1 requirements, worn over splash goggles, is required any time there is a risk of explosion, a splash hazard, or a highly exothermic reaction.
- All manipulations of pyrophoric chemicals must be carried out in a fume hood with the sash in the lowest feasible position or in a glove box to provide additional eye and face protection.

Skin Protection

- Clothing (shirt and long pants) should be cotton or wool. Synthetic clothing is strongly discouraged.
- Appropriate shoes that cover the entire foot (closed-toe, closed-heel, no holes on the top) must be worn.
- Special fire-resistant laboratory coats made from Nomex® or other fire-resistant materials that meet National Fire Protection Association (NFPA) Standard 2112 compliance are required. Laboratory coats must be buttoned and fit properly to cover as much skin as possible.
- If pyrophoric materials will be handled outside of an inert atmosphere glove box (e.g., during reagent handling, reagent transfer, reagent quenching, spill cleanup), a glove made from

inherently flame-retardant (FR) materials is required (e.g., Ansell Kevlar Goldknit or Hanz Extremity Wear Nomex Utility). A chemical-resistant, non-combustible glove (e.g., Neoprene) must be worn over the FR glove to protect the FR glove from chemical contamination.



Figure 1: Properly (top) and improperly (bottom) fitted inner FR Gloves (yellow) and outer neoprene gloves (green).

I. Emergency Procedures

For guidance on spills of pyrophoric and water reactive materials, consult the [CSUS Chemical Hygiene Plan](https://www.csus.edu/campus-safety/environmental-health-safety/_internal/_documents/chemical_hygiene_plan.pdf). https://www.csus.edu/campus-safety/environmental-health-safety/_internal/_documents/chemical_hygiene_plan.pdf

- DO NOT use water to attempt to extinguish a reactive material fire as it can enhance the combustion of some reactive materials, e.g., metal compounds. Do not use a carbon dioxide fire extinguisher on an organolithium fire.
- Do not use combustible materials (paper towels) to clean up a spill, as these may increase the risk of igniting the reactive compound. Dry sand, Met-L-X, soda ash, or lime should be used to completely smother and cover any small spill that occurs.
- If anyone is exposed or on fire, wash with copious amounts of water under a safety shower.
- Use an appropriate extinguishing agent (dry sand, Met-L-X, soda ash or lime) to extinguish pyrophoric/water-reactive material. Using a Class ABC standard dry powder fire extinguisher may be used with some pyrophorics or to manage a collateral fire. Class D extinguishers are recommended for combustible solid metal fires (e.g., sodium, potassium). Never use a fire extinguisher containing water (or one that may develop water over time), carbon dioxide, or

halons with organolithium compounds as they react violently. Review the SDS for the appropriate fire extinguisher or extinguishing agent.

- Call 9-1-1 for emergency assistance and for 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.**

Note: *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 a non-sprinklered building, contact EH&S at (916) 278-2020 immediately.*

Contact Information

Environmental Health and Safety

(916) 278-2020

<https://www.csus.edu/campus-safety/environmental-health-safety/>