Environmental Health and Safety
Tufts University Standard Operating Procedures (SOP) for Pyrophoric Chemicals

Hazards:
Pyrophoric chemicals are liquids and solids that will ignite spontaneously in air or oxygen. They are extremely reactive toward oxygen and in most cases, water, and must never be exposed to the atmosphere. Exposure of these reagents to air could result in spontaneous combustion, which could cause serious burns or other injuries to the person handling the reagent or others in the immediate area. In addition, all combustible materials, including paper products (Kim wipes), should not be allowed to come in contact with any pyrophoric reagent at any time. These chemicals are used in research to catalyze certain reactions and often are incorporated into final products.

Water-reactive chemicals which react violently with water and humidity in the air, such as the alkali metals and metal alkyl hydrides, should be protected by mineral oil or a solvent while being used. If not protected by mineral oil or solvent they should be handled in a glove box.

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.

Good Practices and Personal Protective Equipment (PPE):
Purchase minimal amounts of pyrophoric materials. Date containers upon initial receipt and upon opening. Take note of any printed expiration dates on the container label and dispose of them as required. Many pyrophoric reagents become unstable or more dangerous with age. Investigators should familiarize themselves with technical bulletins, safety videos and other resources available to learn how to transfer liquid pyrophoric.

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. Pyrophoric chemicals should be stored in secondary containers, away from flammables and oxidizers. You may be able to reuse the secondary container provided by the manufacturer. The metal can that each bottle is shipped in, should be retained as a protective container for transporting and storing the bottle of reagent. Some of these materials may need to be kept below threshold temperatures.

Liquid pyrophorics should be stored in sealed containers with PTFE-lined septa to prevent air exposure, and manipulated via syringe or cannula in a chemical fume hood (over a spill tray if possible) with the sash (ideally horizontal) as low as possible. Mineral oil bubblers must be used to release pressure from reagent or reaction vessels. Solid pyrophorics must be handled only in an inert atmosphere glove box or glove bag.

Set up a designated area for work with pyrophoric materials – a chemical fume hood and/or a (dry) glove box (with inert atmosphere, if needed). Incompatible materials should be removed from the area. Remove all excess and nonessential chemicals and equipment from the fume hood or glove box where pyrophoric or water reactive chemicals will be used. Avoid areas with

heat and flames. Keep combustible materials, including paper towels and Kim wipes, away from reactive reagents. A container of powdered lime or sand should be kept within arm's reach (for covering spills). The sash on the fume hood should be kept as low as possible while working with pyrophoric chemicals.

Employees should be aware of the location of all emergency equipment, safety showers, eyewashes, and fire extinguishers (of appropriate Class, see "Spills:" below) and should know how to use it if needed.

Before conducting the actual procedure, always perform a dry run (without the pyrophoric material) to identify and resolve possible safety hazards. Let co-workers and lab personnel know when you will be using a pyrophoric chemical. Work within sight and/or hearing of at least one other person who is familiar with the hazards and written procedures.

Needles used for transfers should be no larger than 16 gauge (to allow septum on reagent bottle to adequately reseal itself) and should be at least 8-12 inches long to reach the bottom of the reagent bottle. Syringe needles must be luer locked. A syringe can be used to transfer small quantities (up to 20ml). The syringe locking needle assembly and the barrel should be capable of handling twice the volume you wish to transfer (i.e. a 50-ml barrel to transfer 25 ml). This same syringe should not be used to do multiple transfers. The cannula method (double tipped needle) should be used to transfer 50 ml or more of the reagent. All glassware should be oven dried or flame dried under high vacuum and purged with argon or nitrogen gas. Needles, cannulas, and glass (not plastic) syringes should be oven dried, and allowed to cool to room temperature in a desiccator with active desiccant. If oven drying, make sure the oven is not humid from drying previous batches of wet glassware.

Personal Protective Equipment (PPE):
Unless work will be performed in a glove box, a 100% Cotton or fire-retardant lab coats must be worn while manipulating quantities of liquid pyrophorics. 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 must not be worn while working with pyrophorics**.

A non-combustible neoprene, leather, Kevlar or fire-retardant gloves are recommended over nitrile gloves (for fire protection). If the reactive material were to ignite and spill onto the hand, nitrile or latex gloves would also ignite and contribute to severe injury.

Appropriate shoes that cover the entire foot (closed toe, closed heel, no holes in the top) must be worn.

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 do 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.

Spills:
Anticipate spills by having the appropriate clean up equipment on hand. The appropriate clean up supplies can be determined by consulting the safety data sheet. This should occur prior to the

use of any pyrophoric chemicals. Spill control materials for pyrophoric chemicals are designed to be inert and will not react with the reagent. The recommended fire extinguisher is a standard dry powder (ABC) type. Many pyrophoric reagents must not be extinguished using a CO_2 fire extinguisher.

Sand or soda ash (powdered lime) should be readily available where work is performed. A container of powdered lime or sand should be kept within arm's reach when working with pyrophoric materials. Also, a small beaker of sand can be used to safely extinguish any small fires occurring at the tips of needles used to transfer liquid pyrophorics.

Powdered lime or sand should be used to completely smother and cover any spill that occurs.

In the event of a spill, alert personnel in the area. Do not attempt to clean-up a large spill of pyrophoric chemicals. Turn off all ignition sources and vacate the laboratory immediately. Call your supervisor and TUPD at 6-6911.

Safety showers: Researchers should familiarize themselves with the location of the two nearest safety showers and eyewash stations both in and outside the lab prior to beginning work with pyrophoric materials.

Disposal: Never return excess chemicals to the original container. Small amounts of impurities may be introduced into the container which may cause a fire or explosion.

A container with any residual material MUST NEVER be opened to the atmosphere. Attempt to use all the reagent in your chemical reaction. If there is unused and unwanted material left over, place the bottle in a secondary container (preferably the original provided by manufacturer) in the satellite accumulation area for disposal by a licensed contractor and notify EHS for disposal.

Examples of pyrophoric & water reactive materials:

-Organo-metallic reagents (Grignard reagents, RMgX, R=alkyl, X=halogen; n, sec, t-butylithium)
-Non-metal Alkyls (tetramethyl silane, tributylphosphine)
-Nonmetal hydride (diethylarsine, diethylphosphine)
-Metal carbonyls (lithium carbonyl, nickel carbonyl, iron pentacarbonyl)
-Gases (arsine, diborane, phosphine, silane, dichlorosilane)
-Certain Silicon halides (dichloromethysilane)

References / Resources:

-Prudent Practices in the Laboratory, Handling and Disposal of Chemicals. National Research Council. 1995.
-Prudent Practices in the Laboratory, Handling and Management of Chemical Hazards. National Research Council. 2011.
- Sigma-Aldrich Technical Bulletin AL-134, *Handling Air-Sensitive Reagents.* http://www.sigmaaldrich.com/etc/medialib/docs/Aldrich/Bulletin/al_techbull_al134.Par.0001.File.tmp/al_techbull_al134.pdf
- Sigma-Aldrich Technical Bulletin AL-164, *Handling Pyrophoric Reagents.*

http://www.sigmaaldrich.com/etc/medialib/docs/Aldrich/Bulletin/al_techbull_al164.Par.0001.File.tmp/al_techbull_al164.pdf
-J.A. Schwindeman, C.J. Woltermann, R.J. Letchford, *Safe Handling of Oranolithium Compounds in the Laboratory.* Chemical Health & Safety, May/June 2002.
-U.S. Department of Energy and Pacific Northwest National Laboratory, *Handling Pyrophoric Reagents*, August 2009, PNNL-18668.
http://www.pnl.gov/main/publications/external/technical_reports/PNNL-18668.pdf
-University of Pennsylvania, Environmental Health and Radiation Safety, General lab safety; *Pyrophoric Chemicals*. http://www.ehrs.upenn.edu/programs/labsafety/chp/sop/pyros.html
-UC Davis, Safety Services, *SafetyNet #135- Procedures for Safe Use of Pyrophoric/Water Reactive Reagents.* http://safetyservices.ucdavis.edu/safetynets/snml/sn135/sn135
-Purdue University, Radiological & Environmental Management*; Laboratory Safety Fact Sheet #37, Safe Use of Pyrophoric/Water Reactive Reagents.*
https://www.purdue.edu/rem/hmm/pyro.htm
-UC San Diego: Blink Topics, Safety. Handling Pyrophoric and Other Highly Reactive Materials:
http://blink.ucsd.edu/safety/research-lab/chemical/specific/pyrophoric.html

Videos: ***If the video does not appear to run properly, please switch to a different web browser (Internet Explorer or Mozilla Firefox) and try again. There may be an issue with Adobe Flash security.***

UC San Diego, Blink, laboratory safety videos: Working with pyrophoric reagents
http://weizman.ucsd.edu/CoursePages/Uglabs/143A_Weizman/EHS/EHS.html
or See "video" parts 1, 2 and 3 under:
http://blink.ucsd.edu/safety/research-lab/chemical/chua/hazard-control-plan/index.html#Pyrophoric-materials

UCLA pyrophoric liquid safety video:
https://www.youtube.com/watch?v=21iC4YEgOAs
Yale University Organolithium safety Training: http://ehs.yale.edu/trainings/organolithium-compounds
UC Irvine; Pyrophorics Safety:
http://www.ehs.uci.edu/programs/sop_library/Pyrophoric/Pyrophorics_combined_works.html

Dow Chemical Company; click on "specialized topics" then "pyrophorics:"
http://safety.dow.com/safety-courses

Suppliers:
This web site has fire resistant cotton lab coats & nomex lab coats;
http://www.safetysupplyamerica.com/c-718-fr-lab-coats.aspx

Nomex flight gloves are found at:
http://blackhawk.com/products/protective-gear/gloves/tactical/aviator-flight-ops-gloves-with-nomex