C3. Safe Handling of Pyrophoric Materials

BACKGROUND

Pyrophoric materials are substances that spontaneously ignite in air at or below 54°C. Exposure to air or moisture can cause these materials to evolve heat, fire, flammable or corrosive byproducts by violent decomposition. Other common hazards include corrosivity, teratogenicity, organic peroxide formation, and damage to the liver, kidneys, and central nervous system. Examples include metal hydrides, finely divided metal powders, non-metal hydride, alkyl compounds, white phosphorus, alloy of reactive materials and organo-metallic compounds.

CONTROLLING THE HAZARDS

Lab supervisors are responsible for ensuring that all personnel working with pyrophoric materials are trained about the hazards and the specific material handling technique and procedure, including emergency response procedures

- If possible, use safer chemical alternatives.
- Prepare a written plan of the work to be performed.
- A Standard Operating Procedure (SOP) and Hazard Assessment should be prepared for each process involving pyrophoric materials.
 - Ensure relevant procedures, technical bulletins and Safety Data Sheets (SDS) have been read and understood **BEFORE** work with pyrophoric reagents, and that the documents are available at all times while handling the material.
- Limit the amount purchased and do not accumulate unneeded reagents.
- On-the-job training must be completed and documented.
- Review emergency procedures; know the location of the safety shower, eyewash, telephone (dial 911), and fire extinguisher.

PERSONAL PROTECTIVE EQUIPMENT

Always wear the proper PPE at all times when handling pyrophoric materials.

Eye protection

- Chemical Splash goggles or safety glasses must be worn whenever handling pyrophoric chemicals.
- A face shield is required any time there is a risk of explosion, large splash hazard or a highly exothermic reaction. Portable shields are also acceptable.

Skin Protection

- Gloves must be worn when handling pyrophoric chemicals. Sigma-Aldrich recommends the use
 of nitrile gloves underneath neoprene gloves.
- A lab coat or apron (not made from easily ignited material like nylon or polyester) must be worn.
 Special fire-resistant lab coats made from Nomex are recommended. Avoid wearing synthetic clothing
- No open toe shoes are allowed.



ENGINEERING CONTROLS

Fume hood

Ensure that all use and handling of pyrophoric liquids is performed in an appropriate glove box or in a chemical fume hood using techniques to ensure isolation from the air/moisture (see Aldrich technical bulletins 134 and 164). Pyrophoric solids must be handled in an appropriate glove box.

Many pyrophoric chemicals release noxious or flammable gases and should be handled in a laboratory hood with the sash down at the lowest feasible position. In addition, some pyrophoric materials are stored under kerosene (or other flammable solvent); the use of a fume hood (or glove box) is required to prevent the release of flammable vapors into the laboratory.

Glove (dry) box

Glove boxes are an excellent device to control pyrophoric chemicals when inert or dry atmospheres are required.

IMPORTANT STEPS TO FOLLOW

- A "dry-run" of the experiment should be performed using low-hazard materials, such as water or solvent, as appropriate.
- Use the "buddy system". Do **not** work alone with pyrophorics.
- Conduct the procedure only after a supervisor has observed the user performing the proper technique unassisted.
- All glassware used for pyrophorics should be oven-dried and free of moisture.
- Keep an appropriate fire extinguisher or extinguishing material close at hand.
- Remove all other flammable material from the hood, as well as any clutter.
- Secure the pyrophoric reagent bottle to a stand.
- Pyrophoric liquid transfer:
 - Sigma-Aldrich recommends the use of a long needle, 1-2 foot, and a syringe that is twice the volume of liquid to be transferred.
 - The syringe needs to be secured so if the plunger blows out of the body, the contents will not splash anyone.
 - Use a syringe to transfer small volumes (< 20 mL). The cannula technique is recommended for larger volumes.

STORAGE

Avoid areas with heat/flames, oxidizers, and water sources. Containers carrying pyrophoric materials must be clearly labeled with the correct chemical name and hazard warning.

Pyrophoric chemicals should be stored under an atmosphere of inert gas or under kerosene, oil, or within a solvent as appropriate (the material must be preserved during storage and while dispensing). Do **NOT** allow pyrophoric chemicals stored in solvent to dry out. Check periodically to ensure there is a visible amount of solvent in the bottle.



DISPOSAL

- Prior to disposal, pyrophoric materials must be transferred to an appropriate reaction flask and destroyed (quenched) by hydrolysis and/or neutralization with adequate cooling. Specific quenching procedures appropriate for the material being handled are to be included in the work written procedure.
- All materials that contain or are contaminated with pyrophoric chemicals should be disposed of as hazardous waste through the Hazardous Waste Inventory System.
- A container with residual material must NEVER be opened to the atmosphere.
- If the pyrophoric chemical was originally stored in solvent and is dried, hydrate the chemical with an appropriate solvent before pick-up; use the same solvent used for the original reagent.

EMERGENCY PROCEDURES

- Keep spill absorbent material within arm's length. Use powdered lime, dry sand, or clay-based kitty litter to completely cover any spill.
- If a person is exposed, or on fire, use the stop, drop, and roll method. A safety shower, a fire blanket, or fire extinguisher are the most effective means of controlling clothing on fire.
- The recommended fire extinguisher is a standard dry powder (ABC) type. Class D extinguishers are recommended for combustible solid metal fires (such as sodium).
- Call 911 for emergency assistance

REFERENCES

Handling air sensitive reagents - Technical Bulletin AL-134. (1997, 3). Retrieved 05 29, 2009, from www.sigmaaldrich.com: http://www.sigmaaldrich.com/etc/medialib/docs/Aldrich/Bulletin/al_techbull_al134
Par.0001. File. tmp/al_techbull_al134.pdf

Handling Pyrophoric Reagents - Technical Bulletin AL-164. (1995, 06). Retrieved 05 29, 2009, from www.SigmaAldrich.com:

http://www.sigmaaldrich.com/etc/medialib/docs/Aldrich/Bulletin/al_techbull_al164.Par.0001.File.tmp/al_techbull_al164.pdf

A <u>fatal 2009 laboratory incident</u> at UCLA involved an accident with t-butyllitium. A <u>detailed account of the accident</u> is available courtesy of the American Chemical Society.

<u>"Safe handling of organolithium compounds in the laboratory"</u>, the Division of Chemical Health and Safety, American Chemical Society.

<u>Pyrophoric Liquids</u>, a safety video produced by the UCLA EHS Department demonstrates how to work with these materials. (12 minutes)

Handling Pyrophoric Materials, a safety video produced by Dartmouth College. (21 minutes)