University Health and Safety

Fact Sheet

Pyrophoric Chemicals Guide

Disclaimer: *In order to use pyrophoric chemicals, potential users must:*

- *Read and fully understood these safe operating procedures*
- *Receive hands-on training from an experienced user familiar with department standards of use*
- *New users of pyrophoric reagents must work under the close supervision of an experienced user, until they have reliably demonstrated proficiency*

Introduction

Pyrophoric chemicals are liquids and solids that have the potential to spontaneously ignite in air at temperatures of 130 °F (54 °C) or below. They are often also considered *corrosive, water reactive,* and have *peroxide forming* properties. Improper use of these materials has resulted in fires, damage to lab equipment, injury and even death in academic laboratories. The increased level of risk involved when working with pyrophoric chemicals calls for additional safety standards to ensure appropriate protection while using these materials. This guidance document should be used as resource for labs performing a risk analysis of their pyrophoric chemical processes when writing lab-specific standard operating procedures (SOPs). It is also intended to raise awareness of the dangers associated with pyrophoric chemicals and help prevent or decrease the severity of future incidents.

What is a pyrophoric material?

Pyrophoric
[pahy-ruh-fawr-ik] [from Greek *purophoros* , "fire-bearing", from *pur* "fire" + *pherein* to "bear"]
A material that is in the solid, liquid or gas phase and has the ability to **spontaneously ignite** in air at temperatures of 130 °F (54 °C) or below without the influence of heat or fire. Pyrophoric gases such as diborane are stored in compressed gas cylinders. Pyrophoric liquids such as *tert*-butyllithium are often metal-(alkyls, aryls, vinyls, carbonyls or hydrides) that are stored in flammable hydrocarbon solvents. Pyrophoric solids such as lithium are often alkali metals and stored under kerosene or oil. Please see **Appendix – List of Pyrophoric Materials** for a more comprehensive list of pyrophoric materials.

Engineering Controls

Glove (dry) box

- A control device that is flushed with inert gas (e.g. nitrogen, argon etc.) and is used for working in inert atmospheres
- *May be required* for certain solid pyrophoric chemicals and *strongly recommended* for liquid and gas pyrophoric chemicals (especially during transfers)

Glove bags

- If access to a glove box is not possible, inexpensive inert atmosphere glove bags are an alternative
- Inert atmosphere glove bags can be purchased through vendors such as Sigma Aldrich

Fume Hood

- Used to control noxious or flammable vapors from solvents used in the storage of pyrophoric reagents or vapors released upon the reaction of pyrophoric chemicals
- *Required* minimum when glove box is not suitable
- Sash must be pulled down as low as possible

Gas Cabinets (*required for pyrophoric gases*)

- Outside each gas cabinet, devices for Remote manual shutdown of pyrophoric gas flow should be provided.
- Automatic shutdown devices for pyrophoric gas flow activated by interlocks tied into fire protection and/or detection should be protected.
- Pyrophoric gas flow, purge, and exhaust systems should have redundant controls that prevent pyrophoric gas from igniting or exploding.
    - These controls include: excess flow valves, flow orifices, mass flow controller sizing, process bypass line control, and automatic gas shutdown.
- Emergency back-up power should be provided for all electrical controls, alarms and safeguards associated with the storage and process systems.
- Mechanical or natural ventilation at a minimum of .00047 cubic meters per .09 square meters of storage and dispensing area should be provided.

Vacuum pump protection [UNT Pyrophoric safety training]

- Any work with pyrophoric chemicals under vacuum must be conducted in fume hood
- Cold traps and filters must be used to prevent particulate release and protect the vacuum pump
- Vacuum exhaust must vent into a fume hood
- Take precautions to prevent implosion of glassware and limit potential damage caused by flying glass and splattered chemicals

Portable shields

- The use of portable shields, whenever available, is recommended as they will protect all occupants and they provide an excellent protection barrier beyond the fume hood sash and regular PPE.

Additional Safety Equipment

Fire Extinguishers

Contact DEHS for advice selecting extinguishers or to receive training. *Do NOT* use extinguishers that contain or generate water, carbon dioxide or halons. They are not suitable for firefighting organolithium compounds as they react violently.

- Class A, B, C (*dry chemical*)
  - For pyrophoric liquids and supporting flammable solvents
  - Must be located within 10 seconds travel time
- Class D (*recommended for certain materials)*
  - For reactive metals

Know the location as it may not be in the same room

Dry chemical or other means of smothering (*strongly encouraged*):

- A container of powdered lime (CaO, calcium oxide), soda ash (Na_2CO_3) or sand (SiO_2) should be within arm's length when working with pyrophoric materials
- Useful to extinguish any small fire that occurs at the syringe tip (aka "pilot light") as a result of residual reagent exposure to air

Eye wash (*required*)

- Must be located within 10 seconds travel time
- Bottle type stations are not acceptable

Safety Shower (*required*)

- Must be located within 10 seconds travel time

Conditions of Use

Reduce quantities and hazards

- Whenever possible, purchase reagents stored in heptane, as it is less hazardous than other hydrocarbon solvents
- Only order and store what is needed
- Dispose of old bottles with excessive precipitates and unreliable concentrations
- Choose less hazardous reagents whenever possible
  (Source: AkzoNobel Pyrophoricity of metal Alkyls)
  - In general for metal alkyls:

Metal Content ↑	Pyrophoricity ↑
Oxygen content ↑	Pyrophoricity ↓
Halogen Content ↑	Pyrophoricity ↓
Solvent vapor pressure ↑(or boiling point ↓)	Pyrophoricity ↑
Temperature ↑	Pyrophoricity ↑

  - Make substitutions like *n*-butyl lithium instead of *t*-butyllithium

- Use reagents with lower concentrations unless a large volume is needed For example, scale versus reagent dilution.. It's best not to have liters of flammable dilution solvent

Prior to beginning work in the laboratory, researchers must:

- Have taken Laboratory Safety Training (http://www.dehs.umn.edu/training_newlabsafety.htm)
- Receive procedure-specific training that is given by a qualified, experienced supervisor that includes:
  - Hazard analysis
  - The location of safety equipment, such as: eyewash, shower, fire extinguishers, alarm pulls, emergency exits
  - Emergency procedures
- Review any standard operating procedures (SOPs) and Safety Data Sheets (SDSs)
- Practice procedural techniques with non-hazardous chemicals prior to working with the actual reagent
- Be supervised the first few times they conduct any work with pyrophoric chemicals

Conditions for use:
The ***unsupervised*** use of pyrophoric chemicals is forbidden outside of normal business hours (7 AM – 5 PM). After hours, there must be at least 2 people present in the laboratory and all people in the space must be aware of what reagent is in use. Each time before beginning work, verify the accessibility of emergency equipment: eyewash, safety shower, fire extinguishers and exits

Required and recommended personal protective equipment (PPE)

Eye Protection

Safety glasses *(required minimum)*

- All safety glasses must meet the ANSI Z-87.1-1989 standard
  - Obtain this information from the manufacturer before purchasing
  - Look for "Z87" inscribed somewhere on the glasses to confirm
- Prescription glasses ONLY if they also meet the ANSI standard if not safety glasses must be worn over them.

Safety goggles are required if there is a splash potential

Skin Protection

Face shields are required when there is risk of explosion, large splash, or highly exothermic reaction

General dress

Skin must be covered and loose items must be secured while working with pyrophoric chemicals to prevent/minimize burns in the case of an exposure. The following items are requirements:

- No open toe and heel shoes
- No shorts, capris or short skirts
- Skin not protected by PPE must be covered by clothing
- No loose fabric
- Clothing made with natural fibers (i.e.: silk, wool or cotton) is recommended over synthetic material as synthetic material becomes molten when on fire and can cause severe burns
- Hair must be tied back

Gloves
Nitrile gloves are the required minimum when working with pyrophoric reagents. Remember that nitrile gloves are combustible and must be removed rapidly if exposed to pyrophoric chemicals.

Nomex® flight/aviator, Kevlar or leather gloves are recommended to be worn under nitrile gloves when working with large volumes of pyrophoric chemicals as they provide flame protection.

Lab coats
A general, *100% cotton lab coat* is the required minimum for working with small quantities of pyrophoric chemicals using recommended engineering controls. If using 100% cotton instead of a flame resistant lab coat adding flame resistant sleeves (separate arm covers) is recommended for providing protection to the most likely exposed area with an inexpensive and one-size option. A *flame-resistant lab coat* is strongly recommended for work with pyrophoric chemicals in a fume hood. *Flame-proof lab coats* are appropriate for any work with pyrophoric chemicals when available. Any work performed outside of a fume hood (strongly not recommended) MUST be performed with a flame-proof lab coat.

When selecting a lab coat, make sure it is appropriately sized for the user (i.e.: closes properly, proper sleeve length etc.). Contaminated lab coats must be cleaned through an appropriate professional service or discarded.

Aprons
Chemical resistant aprons are required for work with large quantities (> 1 L) of pyrophoric chemicals.

Storage

General Incompatibilities

Pyrophoric materials must be stored away from:

- Air
- Oxidizers
- Water (if water reactive)
- Protonating reagents (e.g. alcohols, amines, mercaptans, and acids)
- Any other flammable and combustible materials (e.g. paper, bench liners, and solvents)
- Heat and vibration sources (organolithium compounds must be kept < 25 °C)
- Corrosive materials which are capable of degrading the reagent container

For reagent-specific incompatibilities and storage recommendations, please refer to the Safety Data Sheet (SDS) or, if it is a prepared reagent, refer to any recommendations listed in the protocol.

Solid pyrophoric chemicals

- Store under kerosene or another appropriate barrier such as a dispersion in mineral oil
- Highly pyrophoric solids should always be stored and handled in an inert atmosphere glove box

Liquid pyrophoric chemicals

- Store as a dilution in a hydrocarbon solvent and under inert atmosphere such as nitrogen or argon
- Store at the recommended temperature, most often in a flammable refrigerator or freezer
- If the reagent bottle is not stored in an inert environment, it should be stored in additional secondary containment, such as the original manufacturer's shipping container, to help prevent release
- Liquids stored in solution should be regularly titrated (including before initial use) to confirm concentration
- Always replace caps after use and seal with Parafilm or electrical tape to protect the septa
- Manufacturer storage options for pyrophoric liquids:
    - AcroSeal
    - Aldrich Sure/Seal
    - Oxford/Sure-Seal Valve Cap

Pyrophoric gases

- The materials must be kept in approved gas cabinets
- The size and quantity of pyrophoric gas cylinders should be kept to a minimum
- Remote manual shutdown devices for pyrophoric gas flow should be provided outside each gas cabinet
- Automatic shutdown devices for pyrophoric gas flow activated by interlocks tied into fire protection and/or detection should be protected

- Pyrophoric gas flow, purge, and exhaust systems should have redundant controls that prevent pyrophoric gas from igniting or exploding. These controls include excess flow valves, flow orifices, mass flow controller sizing, process bypass line control, and automatic gas shutdown
- Emergency back-up power should be provided for all electrical controls, alarms and safeguards associated with the storage and process systems
- All process systems components and equipment should be purged with a dedicated inert gas cylinder
- Pyrophoric storage and dispensing areas should be located on the exterior of the building, or in an approved shelter
- Mechanical or natural ventilation at a minimum of .00047 cubic meters per .09 square meters of storage and dispensing area should be provided
- Cylinder orifices with a 0.0006 inch diameter and not to exceed 0.010 inches

Handling

General Principles for Reagent Transfers

Each time prior to transferring reagents, THINK "***Triple A+***" Safety (All-Access-Aware-Plus)

- ***All*** necessary PPE (e.g. chemical resistant gloves, eye protection, lab coat)
- ***Access***ibility of intended eyewash, safety shower, exit and fire extinguisher
- Make sure there is at least one other person in the lab and they are ***Aware*** of what you are about to do and emergency procedures
- ***Plus (+)*** check to make sure your space is free of aqueous, *combustible* and *oxidizin*g materials

Transfer of Pyrophoric Solids

In general, the transfer of pyrophoric solids should be performed in an inert atmosphere glove box. A reagent that is mildly pyrophoric and/or dispersed in mineral oil (such as sodium hydride) may be handled safely in a fume hood in the presence of air. The solid should be weighed in a vessel that is resistant to quenching solvents (e.g. avoid any plastic that will dissolve). The reagent container must be flushed with inert gas before storage.

Weighing an Alkali Metal ***[UCLA Solid pyrophoric chemical SOP]***

1. Using a knife, cut the metal while submerged under oil in the reagent jar. It is best practice to cut small pieces so that slow, deliberate addition to a reaction flask is easy.
2. Use tweezers to transfer from oil covered reagent bottle to rinse flask that contains toluene, hexanes or heptane to rinse off oil.
   a. *AVOID low boiling rinses such as ether and pentane that tend to condense water upon evaporation.*
3. Transfer from rinse flask to a weighed flask of toluene and determine the mass of the metal.

   a. *For the weighed flask, choose higher boiling solvents, such as toluene, to avoid balance fluctuation while weighing.*
   b. *Note- Check with your advisor, if you need a more accurate weight, it is sometimes considered acceptable to weigh a solid such as sodium in a glass dish once the solvent has evaporated. Leaving the solid without the solvent preventing contact with air increases the risk of auto-ignition.*
4. Use tweezers again to transfer from the toluene to desired reaction flask.
5. At the end of the process, the rinse flask along with the toluene-filled weigh flask and the tweezers should be quenched to clean any alkali metal residue.
   a. *See the section below on <u>Preventative Maintenance (Quenching, cleaning and disposal)</u> for guidance.*
6. <u>Special note:</u> Potassium metal is considerably more reactive than lithium or sodium. Upon oxidation, yellow peroxides can form that are shock-sensitive and can explode when handled or cut. If the reagent is old or if significant amounts of yellow crust is visible: *DO NOT USE*! Contact the Hazardous Chemical Waste Program and explain the hazards of what needs to be disposed.

Recommendations for working with hydrides in a dispersion of mineral oil

<u>Potassium hydride (KH)</u> or <u>sodium hydride (NaH)</u> dispersions can be weighed out as solids outside of a glove box. The concentration of the reagent in the dispersion oil needs to be taken into consideration when calculating the final weight. If it is necessary to remove the dispersion oil, this can be done in a glove box or in a fume hood under carefully controlled conditions:

In a fume hood: ***[UCLA Pyrophoric Solid SOP]***

1. Weigh out desired amount of hydride dispersion and seal it in a flask under nitrogen
2. Add dry hexane via syringe, swirl, and let metal hydride settle
3. Slowly syringe off the hexane and carefully discard it into a separate flask containing isopropanol
4. Repeat rinse procedure
5. Note: the rinsed hydride is more reactive and exposure to air and moisture should be avoided

Transfer of Pyrophoric Liquids

By using proper needle and syringe techniques, these reagents can be handled safely in the laboratory without the use of an inert atmosphere glove box. Pyrophoric chemicals that exist as a molar concentration in a hydrocarbon solvent should be titrated prior to use (and upon first use) to confirm the active reagent concentration.

SOP Recommendations

Maximum transfer volumes of pyrophoric liquids via syringe should be determined by the laboratory PI and/or supervisor and documented in procedural SOPs.

- A general recommendation is a transfer volume of 20 to 50 mL is appropriate via syringe
- Larger volumes must be divided into different syringe transfers or must be transferred via cannula

Equipment choice

Syringe choice:

- Transfer methods will vary depending on whether glass or plastic syringes are used
  - Identify which type of syringe is most appropriate before beginning work
  - Training and practice runs should be performed using the syringe that is appropriate for the work and compatible with the reagent
- It is important to ensure that over pressurization of the syringe does not occur as it could blow the plunger out of the syringe causing a spill of the pyrophoric reagent
  - A mineral oil bubbler should always be used with the inert gas line to prevent over pressurization of the system
  - A gas pressure of 3-5 psi is generally recommended
- Any syringe used with pyrophoric reagents need to be gas tight and have a needle-lock mechanism (such as Luer-Lok syringes from Fischer Scientific) to prevent separation of the needle and syringe
- A syringe size of 1.5-2X the reagent volume needed is recommended to prevent over-filling

Needle choice:

- Needles must have a locking mechanism to prevent disconnection from the syringe
- A needle should be long enough to reach the reagent level without tipping the reagent bottle at an extreme angle
- The larger the syringe used, the larger the needle gauge to ensure efficiency
  - The gauge should smaller than 16 gauge to avoid perforating the reagent bottle septum with large holes

General Transfer Setup

- Don the required PPE and confirm that all engineering controls (e.g. fume hood, Schlenk line etc.) are properly functioning
- Check all glassware for cracks and defects (if in doubt, do not use)
- Check needles for blockages by passing dry nitrogen through one end and checking (with a pool of liquid or a Kim wipe) that gas comes out the other end
- Dry all glassware, steel needles and glass syringes (oven dry or flame dry), and flush with an inert gas while cooling
- Ensure both the reagent and the reaction vessel are properly secured with clamps and have proper containment

- Flush inert gas through all vessels, transfer lines, syringes and needles
  - Use 3-5 psi to flush vessels and lines
  - Use a bubbler line to flush the syringe and needle
- Check that a mineral oil bubbler (used to release the excess pressure from the reaction vessels) is connected and functioning
  - Balloons used for air-sensitive reagents are not suitable for pyrophoric reagents

Transfer via Syringe
The single use of a syringe and needle before cleaning is best practice to avoid clogs.

Follow these steps in order: **[Insert photographic guide from Sigma]**

1. Secure the reagent bottle with a clamp and insert a needle from an inert gas line with a mineral oil bubbler into the headspace of the reagent bottle
2. Draw inert gas into the dry syringe and needle, then remove the needle from the septum and depress the plunger to expel the gas
   a. Repeat this step 3X, always remembering to insert the needle into the gas headspace
3. Insert the needle into the liquid reagent and gently pull the plunger to draw liquid into the syringe
   a. Pulling the plunger too fast may cause gas bubbles
4. Do NOT fill the syringe more than 50% of the maximum recommended volume listed in the lab-specific SOP
5. Pull the needle above the reagent liquid level and pull in excess inert gas then invert the syringe, push the plunger to push out gas bubbles and ensure the needle is filled with reagent
6. Adjust reagent amount to the desired volume then draw a barrier of inert gas from the reagent bottle in the needle headspace
   a. This step is especially important for highly pyrophoric liquids such as t-butyllithium and trimethylaluminum
7. Carefully withdraw the needle from the reagent bottle and quickly insert it into a reaction vessel that has been filled with inert gas
8. Dispense the reagent by first pushing out the gas barrier
   a. Remember that a pocket of liquid will remain in the needle and syringe tip
9. Pull in a barrier of inert gas, remove the needle from the reaction vessel and insert it into a quench flask with a cleaning solvent and that has been flushed with inert gas
   a. See the Preventative Maintenance section for quenching and cleaning
   b. Immediately clean and quench the syringe and needle to avoid clogs

Transfer via Cannula (aka double-tipped needle safety)

This method should be used when transferring volumes exceeding the maximum syringe transfer volume (identified in a lab-specific SOP). When using the cannula method, never transfer excess material back into an original container as any impurities will contaminate the reagent and may cause an explosive reaction.

Follow these steps in order: **[Insert photographic guide from Sigma]**

1. Secure the reagent bottle with a clamp and insert a needle from an inert gas line with a mineral oil bubbler into the headspace of the reagent bottle
    a. Gas pressure should be 1-2 psi
2. Quickly insert one end of the double-tipped needle (call this end “A”) into the headspace of the pressurized reagent bottle by puncturing the septum (inert gas should flush though the needle)
3. Insert other end of the double-tipped needle (call this end “B”) into the septum of a sealed, dry flask that contains an inert atmosphere
    a. For measurement purposes, a graduated addition flask may be required
4. Begin the transfer by carefully lowering end A of the cannula beneath reagent liquid level
5. Allow the inert gas pressure to force the reagent up through the needle into the reaction vessel
    a. The speed of reagent flow can be managed by adjusting gas pressure and/or the reaction vessel height
6. When the desired reagent volume has been dispensed, stop the transfer by pulling end A of the needle above reagent liquid level but still within vessel
7. Blow the needle dry by allowing inert gas to continue to pass from the pressurized reagent vessel into the vented reaction vessel
8. Carefully withdraw end B of the needle from the reaction vessel and remove the vent
9. Then withdraw end A of the needle from the reagent vessel then turn off the inert gas
10. Immediately clean the needles to avoid clogs and corrosion

Transfer of Pyrophoric Gas

Pyrophoric gas use

Pyrophoric gasses should only be used after lab-specific training has been passed and the techniques have been demonstrated using an inert gas. Pyrophoric gas should only be used during working lab hours when others are around to help in the case of an accidental release.

Transportation of cylinders

- The cover cap should be screwed on hand tight to protect the valve, until the cylinder is in place and ready for actual use
- Cylinders should never be rolled or dragged

- Large cylinders should be strapped to a properly designed wheeled cart
- Only one cylinder should be handled at a time

Preventative Maintenance (Quenching, Cleaning, Disposal)

Quenching of Pyrophoric Residue

Small amounts of unused pyrophoric reagents must be deactivated by quenching excess reagent and residue. Do not leave containers with residues of pyrophoric materials open to the air, because this is a possible flash fire hazard

The basic procedure for quenching is as follows:

1. Transfer the residue to a reaction flask for neutralization
   a. Depending on the pyrophoricity of the material, the reaction flask may need to be sealed under inert gas with a dilution solvent that is sparged and dry
2. Dilute with copious amounts of a non-reactive, low flammability, higher boiling solvent such as hexane, heptane or toluene
   a. Low boiling solvents can condense water upon evaporation
3. Place the flask in an ice bath, and slowly add isopropanol while stirring, to quench pyrophoric residue
4. Once bubbling slows or stops, slowly add methanol as a more reactive quenching agent to ensure completion
5. Finally, add cold water drop-wise or small ice chips to ensure that no unquenched reagent remains
6. Dispose of as hazardous waste through the University's Hazardous Waste Program
   a. Remember to tag the material as the quench salt products rather than the unreacted pyrophoric
   b. UMN Hazardous Chemical Waste Management Guidebook
   c. Hazardous Waste Group – (612) 626-1604

Cleaning Pyrophoric Reagents from Needles and Syringes

After the use of pyrophoric reagents, it is essential to clean any residual, unreacted material from the syringe and needle to prevent unintentional fires and clogs.

Syringes and needles

1. After the addition of pyrophoric liquids to a reaction flask, remove the needle from the flask and insert it into a septum of a flask sealed under inert gas containing dry dilution solvent such as hexanes, heptane or toluene

2. Draw dilution solvent into the syringe and expel it into a flask containing isopropanol several times
3. Draw clean isopropanol into the syringe and then expel it into the quench flask several times
4. Draw water into the syringe and expel it into the quench flask several times
5. If using glass syringes and/or steel needles, rinse them with a compatible solvent (note acetone may not compatible with rubber gaskets)and air or oven dry before reuse
6. Dispose of the wash solvents with compatible hazardous waste solvents

Cannulas

1. Once a cannula transfer is finished and the cannula is clear of pyrophoric liquid, insert one end of the cannula into a sealed flask (Flask A) containing an inert dilution solvent such as hexanes, heptane or toluene
2. Insert the other end into a sealed flask (Flask B) containing isopropanol and a bubbler outlet
3. Insert a nitrogen inlet into Flask A and lower the cannula into the dilution solvent
   a. This will push the dilution solvent through the cannula and into Flask B containing isopropanol
4. Add isopropanol to Flask A and allow the isopropanol to flow through the cannula into Flask B
5. Add water to Flask A and allow the water to flow through the cannula into flask B
6. Finally, rinse the cannula with acetone and wipe the outside before air or oven drying
7. Dispose of the wash solvents with compatible hazardous waste solvents

Tips for unclogging steel needles

If not cleaned immediately or properly, reusable steel needles may become clogged with salts from the quench of pyrophoric chemicals. Before disposing of a clogged needle, try the below techniques to loosen clogs. Be sure to consult with an experienced lab supervisor before attempting these methods on your own.

- Carefully insert a thin wire into both ends of the needle to loosen salts
- Sonciate the needle in warm water for 5-10 minutes
- Gently heat the length of the steel needle while holding it with tweezers

Disposal of Pyrophoric Solids through the Hazardous Waste Program

- Larger quantities of pyrophoric solid chemicals can be disposed of as hazardous waste without quenching
- Carefully package and label the containers according the University's hazardous waste guidelines (http://www.dehs.umn.edu/hazwaste_chemwaste_umn_cwmgbk_sec2.htm)
- Specifically alert EH&S personnel at the collection location to the hazards of any waste containing pyrophoric chemicals
- If you require assistance, contact the Hazardous Chemical Waste group at (612) 624-1604 and specifically state that you need help with pyrophoric hazardous waste disposal

Emergency Preparation

Spills

In the event of a pyrophoric chemical spill, it is necessary to exert extreme caution due to the probability of spontaneous and ignition of flammable solvents or other materials. [ref: UCLA Chemistry & Biochemistry Procedures for Safe Use of Pyrophoric Solids, 2/2009 Page 4 of 4]

General considerations

- When writing lab-specific SOPs for handling pyrophoric chemicals, it is important to determine, as a group, what is spill size of a reagent is acceptable for staff to handle cleanup
- If a fire occurs that cannot be extinguished by reasonable means, it is important to call 911 immediately and inform the dispatcher that a fire has occurred due to a chemical release

Large Spills

- If anyone is exposed, or on fire, wash with copious amounts of water, ideally in the lab shower
- Call 911 for emergency assistance and inform them that a chemical release has occurred
- Evacuate the spill area
- Mark-off the hazardous area with tape and warning signs or post someone (if it is safe to do so) in order to keep other people from entering
- Locate emergency personnel and provide them with technical advice on the chemicals involved

Small Spills

- In the event of a flash fire, dial 911 and inform the dispatcher that a chemical release has caused a fire
- At any time if emergency assistance is required during the cleanup process, call 911 and inform the dispatcher that a chemical release has occurred
- If anyone is exposed, or on fire, wash with copious amounts of water, ideally in the lab shower
- Call for a coworker to provide backup
- Place a class C fire extinguisher nearby the spill area before cleanup
- Carefully remove nearby flammable materials
- Powdered lime (calcium oxide, CaO) or dry sand should be used to completely smother and cover any spill that occurs
- Carefully quench by slow addition of isopropanol
- After complete quench, double bag spill residues for hazardous waste pickup

General Health Hazards and Toxicity

Eyes: Can cause severe burns to the eyes.
Skin: Can cause severe burns to the skin.
Ingestion: May cause severe and permanent damage to the digestive tract. Can cause severe burns to the gastrointestinal tract. May cause central nervous system depression.
Inhalation: Causes chemical burns to the respiratory tract. Exposure produces central nervous system depression. May cause drowsiness, unconsciousness, and central nervous system depression. Vapors may cause dizziness or suffocation.
Chronic: Repeated exposure can cause nervous system abnormalities with muscle weakness and damage, motor incoordination, and sensation disturbances.

Exposure Limits

See chemical specific SDS

General Emergency Actions

Eyes: Flush eyes at the emergency eyewash station for 30 minutes. Seek medical attention immediately.
Skin: Remove any contaminated clothing, in case of flash fire. Rinse skin with copious amounts of water for at least 15 minutes. If larger areas of skin are affected, rinse under the emergency safety shower for at least 15 minutes. If you experience any burning or irritation thereafter, seek medical attention.
Ingestion: Do NOT induce vomiting. Seek medical attention immediately.
Inhalation: Remove victim from exposure area to fresh air immediately. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Do NOT use mouth-to-mouth resuscitation. Seek immediate medical attention or call 911 if not breathing.

Hazard Correction (Near miss, accident investigation and corrections)

Note: This section will contain recommended follow-up items for near miss and accidents.

Reporting lab accidents and near-accidents can allow others to learn what measures need to be taken to safely run an experiment to prevent a similar situation. Information reported can be used to generate alerts, create safety moments, and stop unsafe situations.

Near miss

Example a small fire starts inside containment, and is controlled by following extinguishing methods. Discuss with your advisor and share with your group. Recommend completing a Learning Experience Report is a document for recording incidents or situations that could have led to incidents (near-misses) that happen in a laboratory setting in a format that can allow others to learn from the experience. These files will be anonymous with a brief description of the incident and the measures that were taken to solve the problem. The student led Joint safety Team from the departments of Chemistry and Chemical Engineering has form for submitting these. **Learning Experience Report Form** (Secure)

Accident reporting

Serious incidents are injuries, fires, explosions or chemical spills & exposures that require external assistance in the form of medical evaluation, fire department, or a chemical spill response team. Reminder Call 911 during.

Your personal health insurance will NOT cover medical expenses that occurred as a result of a work injury. The University will. This is why it is important to complete these forms in the event of personal injury that occurs while at the U.

Injury to a paid employee is reported differently than an unpaid researcher. See below for instructions related an injured paid employee vs injured unpaid individual.

PAID EMPLOYEES (professors, graduate students, post-docs, visiting researchers)- Injury to paid employees is handled as a workers compensation claim (even if no time is missed).

- See UMN Policy Reporting and Managing a Workers Compensation Claim
- The injured employee's supervisor will need to fill out BOTH:
- the online First Report of Injury form, and
- the Supervisor Incident Investigation Report form and email (211@sedgwickcms.com) or fax (952-826-3785) it to the Claims Administrator.

Important Note: If you do NOT receive an email after submitting the online first report of injury the form did not go through. Please contact theOffice of Risk Management for assistance.

UNPAID students, guests & visitors. The form Bodily Injury/Property Damage Incident Report should be emailed or faxed to the University's Office of Risk Management.

Follow-up recommendations

All serious incidents should be reviewed as a group with your safety officer & DEHS. This investigation needs to take place soon after the incident and documentation of the discussion needs to be kept in laboratory records. The Accident Investigation form is used as an outline for discussion and a template for documentation.

Additional Information

For general information regarding the safe use of pyrophoric chemicals, please contact DEHS at (612) 626-6002.

If you have any concerns regarding the stability or testing of a chemical, contact the Hazardous Waste Program at (612) 624-1604.

Resources

[currently a list of documents that have been or should be referenced for this]

Not Voodoo – Pyrophoric Reagents
Not Voodoo – How to titrate alkyl lithiums
UCSD – How to work with pyrophoric reagents
UCLA Solid Pyrophoric Chemicals SOP
UCLA Liquid Pyrophoric Chemicals SOP

Sigma Aldrich:
Technical Bulletin: Handling Air-Sensitive Reagents
Handling Pyrophoric Reagents (95)
Transferring Air-Sensitive Reagents

Other guides:
Chemistry Views – Tips and tricks for the Lab: Air-Sensitive Techniques
Columbia University: Safe use of Pyrophoric Reagents guide

Appendices:
Videos
List of Pyrophoric Materials
Common Manufacturer Seals and Containers
Additional References