Standard Operating Procedure (SOP)

Procedure for Safe Use of Pyrophoric Solids

BUILDING: **ROOM:**

PREPARED BY: **REVISION DATE:**

Experimental Process – Brief Description of the Operation/Experiment:

Rules:
1.) Never work alone with Pyrophoric Solids.

Specialized Training Instructions:

Chemical and Physical Hazards Associate with the Experiment – Before completing this section, please review the UIC Chemicals of Concern form to identify significant chemical hazards involved in this experiment.

Chemical(s):	**Hazard(s):**
	(Ignites Spontaneously when Exposed to Air) **Other Hazards:** Corrosivity Water Reactivity Peroxide Formation

Potential List of Pyrophoric Chemicals

A variety of solids are pyrophoric (spontaneously ignite in air) including (but not necessarily limited to):

1. Finely divided metals (bismuth, calcium, hafnium, iron, magnesium, titanium, uranium, zirconium)

2. Alkali metals (lithium, sodium, potassium, especially sodium potassium alloy – NaK, and even more dangerous are cesium and rubidium)

3. Low valent metals (titanium dichloride)

4. Nonmetals (white phosphorous)

5. Metal hydrides (potassium hydride, sodium hydride, lithium aluminum hydride, uranium trihydride)
6. Nonmetal hydrides (arsine, boranes, germane, phosphine, silane) (Most of these are actually gases.)

7. Partially or fully alkylated derivatives of metal and nonmetal hydrides (diethylaluminium hydride, diisobutylaluminum hydride, dichloro(methyl)silane) (Usually in liquid form or in solution.)

8. Alkylated metals (butyllithium, triethylboron, trimethylaluminum) (Usually in liquid form or in solution.)

9. Alkylated metal alkoxides or halides (dimethylaluminum chloride, diethylethoxyaluminium)

10.Metal carbonyls (dicobalt octacarbonyl, nickel carbonyl)

11. Used hydrogenation catalysts, e.g. Raney Ni, are especially hazardous due to adsorbed hydrogen

12. Copper fuel cell catalysts, e.g. Cu/ZnO/Al2O3 Methanetellurol (CH3TeH)

Handling Pyrophoric Solid Reagents

• Pyrophoric solids are ideally used in a sealed glove box flushed with inert gas.
• Many pyrophoric solids are sold as solutions, or dispersions in mineral oil or are covered with hydrocarbon solvents to facilitate use.
• Mildly pyrophoric solids (such as lithium aluminum hydride and sodium hydride) may be handled in the air for brief periods of time, but the containers must be flushed with inert gas before storage.

Transferring and Weighing Pyrophoric Solid Reagents

• Gather all necessary experimental equipment first to avoid prolonged exposure of pyrophoric solids to air.
• Weighing alkali metals: Cut desired piece of alkali metal under packing oil using a knife. Using tweezers, transfer to adjacent flask containing toluene or heptane to rinse off oil. Use tweezers again to transfer to a weighed flask of toluene and measure weight to determine mass of metal. Use tweezers again to transfer to desired reaction flask.
• AVOID low boiling rinses such as ether and pentane that tend to condense water upon evaporation.

Specific Recommendations for Working with Pyrophoric Solid Reagents

• Lithium Aluminum Hydride reacts violently with water and has a significant heat of solvation. Therefore DO NOT add solvent to dry $LiAlH_4$.
• Potassium metal is considerably more reactive than lithium or sodium.
• Potassium metal oxidizes to potassium oxide (K_2O), potassium peroxide (K_2O_2), and potassium superoxide (KO_2). The yellow peroxides are shock-sensitive and can explode when handled or cut. Therefore dispose of potassium metal as hazardous waste if old or if significant amounts of yellow crust is visible.
• The mineral oil of potassium hydride or sodium hydride dispersions can be rinsed off using a light hydrocarbon solvent such as hexane. This is easily accomplished in a glove box or can be done in a hood UNDER CAREFULLY CONTROLLED CONDITIONS. Weigh out desired amount of dispersion and seal in a flask under nitrogen. Add dry hexane via syringe, swirl, and let metal hydride settle. Slowly syringe off hexane and then carefully discard into a separate flask containing isopropanol. Repeat rinse procedure.
• AVOID low boiling rinses such as ether and pentane that tend to condense water upon evaporation.
• Sodium amalgam, Na(Hg), (or potassium amalgam) is prepared by dissolving sodium into liquid mercury. This highly exothermic process produces the intermetallic compound $NaHg_2$ with enough heat to cause local boiling of the mercury. Thus it must be performed in a hood under dry nitrogen gas. The grey solid produced has the reducing potential of sodium, but is more air stable.

Storage:

Store pyrophoric chemicals under an inert atmosphere or under kerosene as appropriate. Avoid storage areas with heat/flames, oxidizers, and water sources. Container carrying pyrophoric materials must be clearly labeled with the correct chemical name and hazard warning.

ENGINEERING CONTROLS – The following safety equipment or device features must be available.

Fume Hood ☒ **Autoclave** ☐

Biological Safety Cabinet ☐ **Shielding** ☐

Glove Box ☒ **Laminar Flow Hood** ☐

Clean Bench ☐

Toxic Gas Cabinet ☐

Other (Please Explain below) ☐

Further Instructions:

Glove (dry) box
Glove boxes are the preferred engineering controls when working with pyrophoric chemicals.They provide an inert or dry atmospheres, that is required when working with chemicals that can ignite in the air.

Caution!

Always use a glove box over a fume when working with pyrophoric solids.

Fume Hood
Any manipulations of pyrophoric chemicals need to be contained in enclosed systems that are placed inside a fume hood. Remember open air will cause these compounds to ignite. Should you need to work with a pyrophoric compounds inside a fume hood, consult your professor/prinical investigator before beginning work.

Before filling in this section, the UIC Laboratory Hazard Assessment Tool must be completed. Please refer to this document to select appropriate PPE for the experiment.

PROTECTIVE EQUIPMENT – Please list the required PPE for this particular Experiment

Safety Glasses ☐	**Chemical Apron** ☐
Flammable Resistant Lab Coat ☒ **(Nomex Lab Coats Only)**	**Disposable Gowns** ☐
Lab Coat ☒	**Respirator** ☐
Safety Goggles ☒	**Cryogenic Gloves** ☐
Face Shield ☐	**Autoclave Gloves** ☐
Nitrile Glove ☐	**Wire Mesh Gloves** ☐
Butyl Gloves ☐	**Boot Covers** ☐

Further Instructions:

A face shield is required any time there is a risk of explosion, large splash hazard or a highly exothermic reaction. All manipulations of pyrophoric chemicals should occur in a fume hood with the sash in the lowest feasible position.

EMERGENCY EQUIPMENT – Required for handling these hazardous substances

Safety Shower ☒	**Chemical Antidote** ☐
Eyewash ☒	**Emergency Shut-off Switch/Valve** ☐

Fire Extinguisher ☒

Oxygen Sensors/Alarms ☐

Further Instructions:

A **Class C** dry chemical fire extinguisher must be available within 10 seconds travel time from where pyrophoric chemicals are used. Know the location of the nearest **Class D** fire extinguisher. A container of powdered lime (calcium oxide, CaO) should be kept within arm's length when working with a pyrophoric material

Powdered Lime (Calcium Oxide, CaO) or dry sand should be used to completely smother and cover any spill if it occurs.

WASTE DISPOSAL – Please follow EHSO Waste Disposal Guidelines to remove unwanted chemicals after the experiment:

SPECIAL EMERGENCY PROCEDURES – Outline any special emergency procedures unique to this experiment.

GENERAL EMERGENCY PROCEDURES

FIRE/EXPLOSION:

Use R.A.C.E. Rescue, Alarm, Contain, and Evacuate for all building fires.

CHEMICAL SPILL:

Large Spills and Small Spills

There is a large risk of fire and explosion when working with pyrophoric materials. The potential for larges spills to spontaneously ignite is high. The contaminated area should be blocked off from other researchers and if necessary, the affected area should be evacuated as soon as an emergency is determined.

Call 5-5555 for UIC Police on a campus phone OR (312) 355-5555 from a cell phone as needed.

Report the spill to EHSO 6-SAFE (6-7233) or 312-996-7233 and complete an incident report.

Small Spills

Powdered Lime (Calcium Oxide, CaO) or dry sand should be used to completely smother and cover any spill if it occurs.

Note: If there is respiratory irritation associated with the exposure, remove all persons from the contaminated area and contact 6-SAFE or 312-996-7233.

OTHER:
If over exposed to any pyrophoric material, the worker shall be required to shower or flush the affected areas for a minimum of 15 minutes. If the emergency is not life threatening report to UIC Health Services for Medical Evaluation.

University Health Services (MC 684)
835 South Wolcott Avenue, Room E-144
Chicago, Illinois 60612-7338
T 312-996-7420
F 312-413-8485

Life Threatening Emergencies:

Report to University of Illinois Hospital & Health Sciences System
Emergency Room
1740 W Taylor Street
Chicago, IL 60612

Approval and Certification – I approve the use of this SOP for my lab group. I agree to modify this SOP to meet the safety needs of my researchers working in my lab.

PI Signature	Name (Print)	Date

CERTIFICATION – I have read and understand the above SOP. I agree to contact my PI or Lab Manager if I plan to modify this procedure.

Signature	Name (Print)	Date
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Signature	Name (Print)	Date
Signature	**Name (Print)**	**Date**
Signature	**Name (Print)**	**Date**

References

1. OSHA Safety and Health Standards (29CFR1910) - United States Department of Labor, OSHA, Government Printing Office: Washington, DC., (latest edition) http://www.osha.gov/SLTC/healthguidelines/chloroform/recognition.html
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