NJIT New Jersey Institute of Technology

PYROPHORIC SOLIDS

STANDARD OPERATING PROCEDURE

Type of SOP: ☐ Process ☐ Hazardous Chemical ☐ Hazard Class

Department: _____ **Building:** _____ **Room #:**_____

Principal Investigator: _____ **Phone #:**_____

Prepared By: _____ **Email:** _____ **Date:** _____

1. HAZARD OVERVIEW

Researchers should not use pyrophoric reagents until they have read and fully understood these safe operating procedures. However, reading these procedures are not a substitute for hands-on training. **New users of pyrophoric reagents must work under the close supervision of an experienced user.**

In general, **pyrophoric** materials ignite spontaneously when exposed to air. They also tend to be associated with flammable solvents. Other common hazards include corrosivity, water reactivity, peroxide formation, and toxicity.

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

- Finely divided metals *(e.g., bismuth, calcium, hafnium, iron, magnesium, titanium, uranium, zirconium)*
- Alkali metals *(e.g., lithium, sodium, potassium, especially sodium potassium alloy – NaK, and even more dangerous are cesium and rubidium)*
- Low valent metals *(e.g., titanium dichloride)*
- Nonmetals *(e.g., white phosphorous)*
- Metal hydrides *(e.g., potassium hydride, sodium hydride, lithium aluminum hydride, uranium trihydride)*
- Nonmetal hydrides *(e.g., arsine, boranes, germane, phosphine, silane, sodium borohydride) (Most but not all of these are actually gases.)*
- Partially or fully alkylated derivatives of metal and nonmetal hydrides-- usually in liquid form or in solution. *(e.g., diethylaluminium hydride, diisobutylaluminum hydride, dichloro(methyl)silane)*
- Alkylated metals-- usually in liquid form or in solution. *(e.g., butyllithium, triethylboron, trimethylaluminum)*
- Alkylated metal alkoxides or halides *(e.g., dimethylaluminum chloride, diethylethoxyaluminium)*
- Metal carbonyls *(e.g., dicobalt octacarbonyl, nickel carbonyl)*
- Used hydrogenation catalysts, e.g. Raney Ni, are especially hazardous due to adsorbed hydrogen

Reference: University of California, Santa Barbara - Environmental Health & Safety

- Copper fuel cell catalysts, e.g. Cu/ZnO/Al2O3 Methanetellurol (CH3TeH)
- Finely divided Iron sulfides (FeS, FeS2, Fe3S4), Potassium sulfide (K2S), Aluminum phosphide (AlP)

2. PERSONAL PROTECTIVE EQUIPMENT (PPE)

At minimum, eye protection, a flame-resistant lab coat, and gloves are required. Additional or more protective PPE may be required. Please refer to the NJIT Chemical Hygiene Guide and Hazard Assessment Form to determine the proper PPE for handling corrosive materials.

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3. ENGINEERING/VENTILATION CONTROLS

In general, pyrophorics should always be used in a properly functioning fume hood. Many pyrophoric chemicals release noxious or flammable gases and should be handled in a chemical fume hood. In addition, some pyrophoric materials are stored under kerosene or other flammable solvent. Therefore, the use of a fume hood (or glove box) is required to prevent the release of flammable vapors into the laboratory. Gloveboxes are an excellent device to control pyrophoric chemicals when inert or dry atmospheres are required.

Please review the NJIT Chemical Hygiene Guide and the Safe Chemical Fume Hood Use Guide for information on the proper use of a chemical fume hood and criteria for implementing engineering controls.

☐ Chemical Fume Hood ☐ Glovebox ☐ Biological Safety Cabinet ☐ Other _____

Room Location of Unit(s): _____

4. SPECIAL HANDLING PROCEDURES AND STORAGE REQUIREMENTS

Before working with pyrophoric reagents, read the relevant Safety Data Sheets (SDS) and understand the hazards. **The SDS must be reviewed before using an unfamiliar chemical and periodically as a reminder.** Set up your work in a laboratory fume hood or glovebox and **ALWAYS wear the appropriate PPE.**

A. Handling Pyrophoric Solid Reagents

- Pyrophoric solids are ideally used in a sealed glovebox 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.

Reference: University of California, Santa Barbara - Environmental Health & Safety

B. 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.

C. Specific Recommendations for Working with Pyrophoric Solid Reagents

- Lithium Aluminum Hydride (LiAlH4) reacts violently with water and has a significant heat of solvation. Therefore, **do not** add solvent to dry LiAlH4. Instead, slowly add LiAlH4 to anhydrous solvent in the reaction flask. The initial small amount of LiAlH4 will react with any trace amounts of water.
- Potassium metal is considerably more reactive than lithium or sodium.
- Potassium metal oxidizes to potassium oxide (K2O), potassium peroxide (K2O2), and potassium superoxide (KO2). **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 a significant amount 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 fume 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 NaHg2 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.

D. Storage

- Store pyrophoric chemicals under an inert atmosphere or under kerosene as directed by the manufacturer's instructions
- **AVOID** storage areas with heat/flames, oxidizers and water sources

Reference: University of California, Santa Barbara - Environmental Health & Safety

5. INCIDENTS AND ACCIDENTS

Please review the SDS, verify with the manufacturer, or contact EHS for proper spill response. If it is safe to do so, prevent the spill from spreading be applying powdered lime or other acceptable material around the spill perimeter. Contact NJIT Public Safety to activate emergency response personnel.

Laboratory personnel are to report all occupational injuries or illnesses to Faculty/PI as soon as practical. The Faculty/PI and laboratory personnel must submit the required paperwork to NJIT EHS Department. See the Emergency Response Guidelines posted in the laboratory or Emergency Procedures section of the NJIT CHG for proper procedures involving an injury, exposure, fire, or release/spill of a hazardous material.

In the event of an emergency, DIAL 9-1-1 to activate emergency response personnel.

Eyewash

Suitable facilities for quick drenching or flushing of the eyes should be within 10 seconds travel time for immediate emergency use. Bottle type eyewash stations are not acceptable.

Safety Shower

A safety shower should be available within 10 seconds travel time from where pyrophoric chemicals are used. These can also be used in the event of a clothing fire.

Fire Extinguisher

- ABC and CO2 extinguishers can cause some pyrophorics to react more vigorously.
- 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 can be used to cover spills and slow the reaction with air/humidity.

6. SPILL AND DECONTAMINATION

Wear proper PPE. Please review the SDS, verify with the manufacturer, or contact EHS for appropriate decontamination procedures. Dispose of all used contaminated disposables in the appropriate waste stream following the Waste Disposal Section of the NJIT CHG.

Decontamination Solution(s): _____

Additional Spill / Decontamination Requirements:

7. WASTE DISPOSAL

Unless the material is still in the original vendor's container, pyrophorics generally need to be "quenched" before giving to the EHS Department for disposal.

Reference: University of California, Santa Barbara - Environmental Health & Safety

Disposal of Pyrophoric Solid Reagents by Quenching

Small amounts of unused or unwanted pyrophoric materials must be destroyed by careful quenching of the residue. Transfer the materials to an appropriate reaction flask for hydrolysis and/or neutralization. Dilute significantly with an unreactive solvent such as heptane or toluene and place the flask in an ice water cooling bath. Slowly add isopropanol to quench pyrophoric materials. Upon completion, add methanol as a more reactive quenching agent to ensure completion. Finally, add water dropwise to make sure there are no pockets of reactive materials. Dispose of as hazardous waste.

- Alternatively, reactive substances can be quenched by slowly adding the dilute solution to dry ice, then adding a mildly reactive quenching agent such as methanol.
- **AVOID** low boiling diluents such as ether and pentane that tend to condense water upon evaporation.
- **Do not** leave containers with residues of pyrophoric materials open to the atmosphere due to uncontrolled ignition.

Follow the practices and procedures in accordance with the NJIT Laboratory Waste Management Program to properly dispose of waste.

Additional Waste Disposal Requirements:

8. PRIOR APPROVAL/REVIEW

9. DESIGNATED USE AREA

Designated Use Area Location(s): _____

10. SAFETY DATA SHEETS

Location of SDS: _____

11. LAB-SPECIFIC INFORMATION (required) *(Examples of appropriate content)*

Reference: University of California, Santa Barbara - Environmental Health & Safety