Safe Method of Use for Highly Hazardous Compounds

Safety Guidelines for Pyrophoric Solids

(Courtesy of Department of Chemistry, University of Auckland)

Researchers **shall** not use pyrophoric reagents until they have read and fully understood these safe operating procedures. However, reading these procedures does not substitute for hands-on training.

New users of pyrophoric reagents **must** work under the close supervision of an experienced user.

A. Scope

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

- Finely divided metals (bismuth, calcium, hafnium, iron, magnesium, titanium, uranium, zirconium)
- Alkali metals (lithium, sodium, potassium, especially sodium potassium alloy – NaK, and even more dangerous are cesium and rubidium)
- Low valent metals (titanium dichloride)
- Nonmetals (white phosphorous)
- Metal hydrides (potassium hydride, sodium hydride, lithium aluminum hydride, uranium trihydride)
- Nonmetal hydrides (arsine, boranes, germane, phosphine, silane) (Most of these are actually gases.)
- Partially or fully alkylated derivatives of metal and nonmetal hydrides (diethylaluminium hydride, diisobutylaluminum hydride, dichloro(methyl)silane) (Usually in liquid form or in solution.)
- Alkylated metals (butyllithium, triethylboron, trimethylaluminum) (Usually in liquid form or in solution.)
- Alkylated metal alkoxides or halides (dimethylaluminum chloride, diethylethoxyaluminium)
- Metal carbonyls (dicobalt octacarbonyl, nickel carbonyl)
- Used hydrogenation catalysts, e.g. Raney Ni, are especially hazardous due to adsorbed hydrogen
- Copper fuel cell catalysts, e.g. $Cu/ZnO/Al_2O_3$ Methanetellurol (CH_3TeH)
- Finely divided Iron sulfides (FeS, FeS_2, Fe_3S_4), Potassium sulfide (K_2S), Aluminum phosphide (AlP)

B. Hazards

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

BEFORE working with pyrophoric reagents, read the relevant Material Safety Data Sheets (MSDS) and understand the hazards. The MSDS **must** be reviewed before using an unfamiliar chemical and periodically reviewed as a reminder.

Set up your work in a laboratory fumehood or glove box and ALWAYS wear the appropriate protective equipment.

1. Eye Protection

- Chemical splash goggles or safety glasses **must** be worn whenever handling pyrophoric chemicals. Ordinary prescription glasses will NOT provide adequate protection unless they also meet this standard. When there is the potential for splashes, goggles must be worn, and when appropriate, a face shield added.

- 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 which pose this risk **must** occur in a fumehood with the sash in the lowest feasible position. Portable blast shields, which provide protection to all laboratory occupants, are advisable.

2. Skin Protection

- Gloves must be worn when handling pyrophoric chemicals. Nitrile gloves should be adequate for handling small quantities of most of these in general laboratory settings but they are combustible. Heavy chemical-resistant gloves are required for working with large quantities.

- *A flame resistant lab coat **must** be worn*.

- A chemical-resistant apron worn over the lab coat is required for working with large quantities.

- As part of normal lab protocol, no open toe shoes are allowed.

C. Designated Work Area

Suitable facilities for quick drenching or flushing of the eyes **must** be within 10 seconds travel time for immediate emergency use.

1. Safety Shower

A safety or drench shower **must** be available within 10 seconds travel time from where pyrophoric chemicals are used.

2. Fumehood

- Many pyrophoric chemicals release noxious or flammable gases and should be handled in a laboratory hood.

- In addition, some pyrophoric materials are stored under kerosene (or other flammable solvent), therefore the use of a fumehood (or glove box) is required to prevent the release of flammable vapours into the laboratory.

3. Fire Extinguisher

- A dry powder fire extinguisher **must** be available within the immediate area where pyrophoric chemicals are used.

- A container of powdered lime (calcium oxide, CaO) or dry sand **must** be kept within easy reaching distance when working with a pyrophoric material.

4. Glove (dry) Box

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

D. Protocols

1. 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 in a desiccator.

2. Transferring and Weighing Pyrophoric Solid Reagents

- Set up all necessary experimental equipment first to avoid prolonged exposure of pyrophoric solids to air.

- AVOID low boiling rinses such as ether and pentane that tend to condense water upon evaporation.

3. 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 alkali metal to a weighed flask of toluene and measure weight to determine mass of metal.

- Use tweezers to transfer to desired reaction flask.

4. 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 $LiAlH_4$. Instead, slowly add $LiAlH_4$ to anhydrous solvent in the reaction flask. The initial small amount of $LiAlH_4$ will react with any trace amounts of water.

- 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.

5. Storage

- Store pyrophoric chemicals under an inert atmosphere or under kerosene as appropriate.

- Avoid storage areas with heat/flames, oxidizers, and water sources.

- Containers carrying pyrophoric materials must be clearly labelled with the correct chemical name and hazard warning.

6. Disposal of Pyrophoric Solid Reagents by Quenching

- **Please note specific recommendations in section 4 above.**

- 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 the risk of uncontrolled ignition.

- When using a sodium press, ensure the attachments are all fully quenched when you are finished. This requires the removal of all traces of compressed sodium from the press and careful quenching with isopropanol.

7. Disposal of Pyrophoric Solid Reagents as Hazardous Waste

- Larger quantities of pyrophoric solid chemicals should be disposed of as hazardous waste.
- Carefully package and label the wastes.
- DO NOT attempt to quench large amounts of pyrophoric solids – leave it to the professional disposal companies

E. Emergency Procedures

1. Spill – Large

- Exercise extreme caution due to potential spontaneous combustion.
- Exercise extreme caution due to potential ignition of flammable solvents or other materials.
- If anyone is exposed, or on fire, wash with copious amounts of water, ideally in the lab shower.
- Call 111 for emergency assistance.
- Evacuate the spill area.
- Post someone or mark-off the hazardous area with tape and warning signs to keep other people from entering.
- Provide emergency personnel with technical advice on the chemicals involved.

2. Spill – Small

- Exercise extreme caution due to potential spontaneous combustion.
- Exercise extreme caution due to potential ignition of flammable solvents or other materials.
- 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 fire extinguisher nearby.
- 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 via stores.

- Call 111 for emergency assistance if necessary.