Environmental Health & Safety

Pyrophoric Handling Procedure

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Safe Use of Pyrophoric and Water Reactive Reagents

Introduction

Pyrophoric and water reactive materials can ignite spontaneously on contact with air, moisture in the air, oxygen, or water. Failure to follow proper handling procedures can result in fire or explosion, leading to serious injuries, death and/or significant damage to facilities. This document describes the hazards, proper handling, disposal and emergency procedures for working with pyrophoric and water reactive materials.

Any handling of a pyrophoric/water reactive material is high risk and must be controlled with adequate system design, direct supervision and training. These tasks are two person tasks and workers should not work alone.

Examples of Pyrophoric/Water Reactive Materials

- Metal alkyls and aryls: Alkyl lithium compounds; tert-butyl lithium
- Metal carbonyls: Lithium carbonyl, nickel tetracarbonyl
- Group I (Alkali) metals: Lithium, potassium, sodium, sodium-potassium alloy (NaK), rubidium, cesium, francium
- Metal powders (finely divided): Cobalt, iron, zinc, zirconium
- Metal hydrides: Sodium hydride, lithium aluminum hydride
- Nonmetal hydrides: Diethylarsine, diethylphosphine
- Non-metal alkyls: R_3B, R_3P, R_3As; tetramethyl silane, tributyl phosphine
- White and red phosphorus
- See Appendix A for an additional list.

Hazards

Because these reagents ignite on contact with air and/or water, they must be handled under an inert atmosphere and in such a way that rigorously excludes air/moisture. Some are toxic and many come dissolved or immersed in a flammable solvent. Other common hazards include corrosivity, teratogenicity, water reactivity, or peroxide formation, and may damage to the liver, kidneys, and central nervous system.

Controlling the Hazards

BEFORE working with pyrophoric or water reactive reagents, read the relevant Material Safety Data Sheets (MSDS), technical bulletins, and guidance documents to understand how to mitigate the hazards. The MSDS must be reviewed before using an unfamiliar chemical and periodically as a reminder. Users of reactive materials must complete the Particularly hazardous Substance (PHS) protocol form certifying they be trained in proper lab technique by or under the supervision of their Principal Investigator. This certification verifies the users demonstrated proficiency.

No one should work alone with these materials. Experiments should be planned so that this work is not done off hours, when there are fewer people around to help. ALWAYS wear the appropriate personal protective equipment.

Remove all excess and nonessential chemicals and equipment from the fume hood or glove box where pyrophoric or water reactive chemicals will be used. This will minimize the risk if a fire should occur. Keep combustible materials, including paper towels and Kimwipes, away from reactive reagents.

Keep the amount of pyrophoric or water reactive material present in the lab to the smallest amount practical. Use and handle the smallest quantity practical. It is better to do multiple transfers of small volumes than attempt to handle larger quantities at once.

Personal Protective Equipment (PPE)

Eye Protection

- Chemical splash goggles or safety glasses must be worn whenever handling pyrophoric chemicals. 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 should occur in a fume hood with the sash in the lowest or most protective feasible position. Portable shields, which provide protection to all laboratory occupants, should also be used as necessary.

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. However, they are combustible, and heavy chemical-resistant gloves or Nomex and related Aramid fiber gloves may be appropriate for working with large quantities. Review the MSDS and contact EHS for advice on appropriate gloves.
- A flame resistant lab coat must be worn when working with pyrophoric and water reactive chemicals. Lab coats need to be buttoned and fit properly to cover as much skin as possible. Clothing, shirt and pants, should be cotton or wool. Synthetic clothing is strongly discouraged in laboratories where pyrophoric chemicals are used**.**
- A chemical-resistant apron worn over the lab coat is required for working with large quantities.
- Appropriate shoes that cover the entire foot (closed toe, closed heel, no holes in the top) must be worn in all laboratories.

Eyewash/Safety Showers

- An ANSI approved eyewash station that can provide quick drenching or flushing of the eyes must be immediately available within 10 seconds travel time for emergency use.
- An ANSI approved safety drench shower should be available within 10 seconds travel time from where pyrophoric chemicals are used.
- Ensure that lab personnel know the locations of the eyewashes and safety showers and know how to activate them in the event of an emergency.

Fume Hood

- Many reactive chemicals release noxious or flammable gases upon decomposition and should be handled in a laboratory hood. In addition, some pyrophoric materials are stored under flammable solvents, and 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. Anyone working in a glove box must be trained on the standard operating procedures for the box and review these SOPs with their Principal Investigator prior to beginning work.

Fire Extinguishers

An ABC dry powder extinguisher is appropriate for many of these reagents, however Class D fire extinguishing materials such as Met LX are needed if pyrophoric or water reactive metals such as sodium or potassium are used. These materials must be available within 10 seconds travel time from where chemicals are being handled.

- Know the location of the nearest appropriate fire extinguisher or extinguishing material before beginning work with pyrophoric or water reactive material.
- Anyone who works with pyrophoric material or water reactive chemicals needs to be trained on the selection and use of these materials by the Carnegie Mellon Fire Safety staff. Met LX is available through the EHS office.

Emergency Procedures

Personal Contamination

Be aware of the location of the nearest emergency shower and know how to operate it. Ensure that this shower is within 75 feet of the location where the material is being handled (approximately 10 second travel time).

Go to the nearest emergency shower if contaminated or on fire. Yell for assistance and rinse for 15 minutes, removing all articles of clothing to ensure contaminate is completely removed. These are drench showers that emit 20 gallons/minute of cool water, and will effectively wash off any contaminate or extinguish burning clothing.

Small Spill

Exert extreme caution due to potential spontaneous combustion and potential ignition of flammable solvents or other materials in the area.

- Call for a coworker to provide backup.
- Place the appropriate fire extinguisher nearby.
- Carefully remove nearby flammable materials.
- A container of Met LX should be kept outside of the hood but within close when working with a reactive material. This can be used to completely smother and cover any spill that occurs. Do not use combustible materials (paper towels) to clean up a spill, as these may increase the risk of igniting the reactive compound.
- Carefully quench by slow addition of isopropanol.
- After complete quench, double bag spill residues for hazardous waste pickup.

Call 8-2323 for emergency assistance if necessary and have them notify EHS

Larger Spill

Exert extreme caution due to potential spontaneous combustion and potential ignition of flammable solvents or other materials in the area.

- **If anyone is exposed, or on fire, wash with copious amounts of water at the nearest emergency shower.**
- Call 8-2323 for emergency assistance and have them notify EHS.
- 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.

Fire

If anyone is exposed, or on fire, wash with copious amounts of water at the nearest emergency shower.

- DO NOT use water to attempt to extinguish a reactive material fire.
- The recommended fire extinguisher for most reagents is a standard dry powder (ABC) type. Class D extinguishers are recommended for combustible solid metal fires (e.g, sodium, lithium aluminum hydride). Contact the Carnegie Mellon Fire Safety staff and review the MSDS for the appropriate fire extinguisher selection and training information on their use.
- Call 8-2323 for emergency assistance and for assistance with all fires, even if extinguished.
- Report all fires to EHS.
- Pyrophoric gas releases and associated fires should be extinguished by remotely stopping the gas flow. Never attempt to put out a gas fire if the gas is flowing.

Transportation Though Building

- Newly received packages of pyrophoric chemicals should be transported through our buildings in the same packaging designed for interstate transport. Containers destined for storage should not be unpacked until they can be transferred into a desiccators or other appropriate storage area. Materials should be unpacked for use and then transferred to a dry box or a chemical hood and used as instructed.

Storage

- Use and store minimal amounts of reactive chemicals. Do not store reactive chemicals with flammable materials or in a flammable liquids storage cabinet.
- Store reactive materials as recommended in the MSDS. An inert gas-filled desiccator or glove box may be suitable storage locations for most materials.
- If pyrophoric or water reactive reagents are received in a specially designed shipping, storage or dispensing container (such as the Aldrich Sure/Seal packaging system) ensure that the integrity of that container is maintained.
- Ensure that sufficient protective solvent, oil, kerosene, or inert gas remains in the container while the material is stored.
- NEVER return excess chemical to the original container. Small amounts of impurities introduced into the container may cause a fire or explosion.

Disposal of Pyrophoric Reagents

- Any container with a residue of reactive materials should never be left open to the atmosphere.
- Any unused or unwanted reactive materials must be destroyed by transferring the materials to an appropriate reaction flask for hydrolysis and/or neutralization with adequate cooling.
- The empty container should be rinsed three times with an inert dry COMPATIBLE solvent; this rinse solvent must also be neutralized or hydrolyzed. The rinse solvent must be added to and removed from the container under an inert atmosphere.
- After the container is triple-rinsed, it should be left open in back of a hood or ambient atmosphere at a safe location for at least a week.
- The empty container, solvent rinses and water rinse should be disposed as hazardous waste and should not be mixed with incompatible waste streams.

Disposal of Pyrophoric or Water Reactive Contaminated Materials

- All materials – disposable gloves, wipers, bench paper, etc. - that are contaminated with pyrophoric chemicals should be disposed as hazardous waste.
- The contaminated waste should not be left overnight in the open laboratory but must be properly contained to prevent fires.

Appendix A **PYROPHORIC MATERIALS**

Pyrophoric materials react with air, or with moisture in air. Typical reactions which occur are oxidation and hydrolysis, and the heat generated by the reactions may ignite the chemical. In some cases, these reactions liberate flammable gases which makes ignition a certainty and explosion a real possibility.

Examples of pyrophoric materials are shown below. (List may not be complete)

(a) Pyrophoric alkyl metals and derivatives

Groups
Dialkytzincs
Diplumbanes
Trialkylaluminiums
Trialkylbismuths

Compounds
Bis-dimethylstibinyl oxide
Bis(dimethylthallium) acetylide
Butyllithium
Diethylberyllium
Diethylcadmium
Diethylmagnesium
Diethylzinc
Diisopropylberyllium
Dimethylberyllium
Dimethylbismuth chloride
Dimethylcadmium
Dimethylmagnesium
Dimethylmercury
Dimethyl-phenylethynylthallium
Dimethyl-1-propynylthallium
Dimethylzinc
Ethoxydiethylaluminium
Methylbismuth oxide
Methylcopper
Methyllithium
Methylpotassium
Methylsilver
Methylsodium
Poly (methylenemagnesium)
Propylcopper
Tetramethyldistibine
Tetramethyllead
Triethylantimony
Triethyl bismuth
Triethylgallium
Trimethylantimony
Trimethylgallium
Trimethylthallium
Trivinylbismuth
Vinyllithium

(b) Pyrophoric carbonyl metals
Carbonyllithium
Carbonylpotassium
Carboylsodium
Dodecacarbonyldivanadium
Dodecacarbonyltetracobalt
Dodecacarbonyltriiron
Hexacarbonylchromium
Hexacarbonylmolybdenum
Hexacarbonyltungsten
Nonacarbonyldiiron
Octacarbonyldicobalt
Pentacarbonyliron
Tetracarbonylnickel

(c) Pyrophoric metals (finely divided state)

Caesium
Calcium
Cerium
Chromium
Cobalt
Hafnium
Iridium
Iron
Lead
Lithium
Manganese
Nickel
Palladium
Platinum
Plutonium
Potassium
Rubidium
Sodium
Tantalum
Thorium
Titanium
Uranium
Zirconium

Alloys
Aluminium-Mercury
Bismuth-Plutonium
Copper-Zirconium
Nickel-Titanium

(d) Pyrophoric metal sulphides
(Ammonium sulphide)
Barium sulphide
Calcium sulphide
Chriomium (II) sulphide
Copper (II) sulphide
Diantimony trisulphide
Dibismuth trisulphide
Dicaesium selenide
Dicerium trisulphide
Digold trisulphide
Europium (II) sulphide
Germanium (II) sulphide
Iron disulphide
Iron (II) sulphide
Manganese (II) sulphide
Mercury (II) sulphide
Molybdenum (IV) sulphide
Potassium sulphide
Rhenium (VII) sulphide
Silver sulphide
Sodium disulphide
Sodium polysulphide
Sodium sulphide
Tin (II) sulphide
Tin (IV) sulphide
Titanium (IV) sulphide
Uranium (IV) sulphide

(e) Pyrophoric alkyl non-metals
Bis-(dibutylborino) acetylene
Bis-dimethylarsinyl oxide
Bis-dimethylarsinyl sulphide
Bis-trimethylsilyl oxide
Dibutyl-3-methyl-3-buten-1-Yniborane
Diethoxydimethylsilane
Diethylmethylphosphine
Ethyldimthylphosphine
Tetraethyldiarsine
Tetramethyldiarsine
Tetramethylsilane
Tribenzylarsine
mixo-Tributylborane
Tributylphosphine
Triethylarsine
Triethylborane
Triethylphosphine
Triisopropylphosphine
Trimethylarsine
Trimethylborane
Trimethylphosphine

(f) Pyrophoric alkyl non-metal halides
Butyldichloroborane
Dichlorodiethylsilane
Dichlorodimethylsilane
Dichloro(ethyl)silane
Dichloro(methyl)silane
Iododimethylarsine
Trichloro(ethyl)silane
Trichloro(methyl)silane
Trichloro(vinyl)silane

(g) Pyrophoric alkyl non-metal hydrides
Diethylarsine
Diethylphosphine
Dimethylarsine
1,1-Dimethyldiborane
1,2-Dimethyldiborane
Dimethylphosphine
Ethylphosphine
Methylphosphine
Methylsilane