Pyrophoric & Water-Reactive Chemicals

Introduction

Pyrophoric liquids and solids spontaneously ignite within 5 minutes after coming into contact with air. Water-reactive chemicals become spontaneously flammable or emit flammable gases in potentially dangerous quantities upon contact with water, steam or moisture. The reactive nature of these chemicals makes proper training, handling, storage, and control measures critical to ensuring the health and safety of researchers. Failure to comply with safety measures can lead to fires, explosions, property damage and serious injuries or even death. The purpose of this document is to offer guidance on the safe use of pyrophoric chemicals and water-reactive chemicals at Central Michigan University (CMU). Any handling of a pyrophoric or 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.

For pyrophoric materials, oxidation of the compound by oxygen or moisture in air proceeds so rapidly that ignition occurs. Many finely divided metals are pyrophoric, and their degree of reactivity depends on particle size, the presence of moisture, and the thermodynamics of metal oxide or metal nitride formation. Other reducing agents, such as metal hydrides, alloys of reactive metals, low-valent metal salts, and finely divided iron sulfides are also pyrophoric.

Hazards

The main hazard associated with pyrophoric and water-reactive chemicals is **fire** upon contact with air or moisture. The high level of **reactivity** associated with these chemicals requires them to be handled in inert atmospheres, free of ignition sources. The hazards associated with these chemicals is exacerbated by the fact that many are stored in highly flammable solvents (e.g., diethyl ether, hexane, pentane, tetrahydrofuran, etc.), further increasing the risk and severity of fires.

In addition to reactivity and flammability, many of these chemicals are also classified as acutely toxic, corrosive, reproductive toxins, peroxide-forming agents or capable of damaging the liver, kidneys, and central nervous system. Safety data sheets (SDSs) should indicate the hazards pertaining to specific pyrophoric or water-reactive chemicals being used in the lab. Strict adherence to standard operating procedures and safe work practices should be followed to ensure safe usage.

Administrative Controls

BEFORE working with pyrophorics, review the Safety Data Sheets (SDS), technical bulletins, and guidance documents to understand how to manage the hazards.

Principal investigators must develop and implement Standard Operating Procedures (SOP's) for work practices and procedures involving pyrophoric chemicals as well as other highly reactive chemicals. The principle investigator trains staff members/students accordingly on proper techniques. Once trained, the principle investigator and staff members/students will sign off on the SOP and forward a copy to the Office of Laboratory and Field Safety office (Foust Hall 108).

All tasks having potential for occupational pyrophoric exposure will only be conducted by competent staff who have received appropriate training (Laboratory Safety Training as well as

task- specific training) regarding the specific health and safety risks, SOPs, and procedures to be followed in the event of an exposure incident.

Whenever possible, principal investigators should consider the use of less hazardous, alternative chemicals. Use pilot reactions to confirm the appropriate safeguards are present and operable before scaling up.

No one should work alone with pyrophorics. Experiments should be planned so that this work is not done during 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 Kimwipe® tissues, away from reactive reagents.

Keep the amount of pyrophoric 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.

Remove spark sources such as heater guns from area around reaction.

Handle all reactive chemicals with extreme care, and store them away from incompatible chemicals.

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.

Engineering Controls

Designated Areas –

Fume Hoods - Many pyrophoric chemicals release noxious or flammable gases and must be handled in a ventilated hood. In addition, many pyrophoric chemicals are either suspended in a combustible solvent such as Kerosene, or are dissolved in highly flammable organic solvent such as hexane, heptane, or ethers. Fume hoods are required to prevent the release of flammable vapors or gases into the laboratory.

Glove (Dry) Boxes - An inert atmosphere dry box is the best location for handling pyrophoric materials because of the lack of oxygen or moisture. Anyone working in a glove box must be trained on the standard operating procedures for the box. These SOPs should be reviewed prior to beginning work.

If a glove box is not available, manipulation of these reagents via syringe or cannula should always be conducted in a certified chemical fume hood, over a spill tray if possible, with the sash at the lowest practicable working height. Needles should be equipped with locking mechanisms to prevent accidental disconnection and release of reagents.

Portable blast shields placed inside the fume hood can be used as a protection barrier.

Safety Equipment and Personal Protective Equipment

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

Safety Shower - A safety or drench shower must be available within 10 seconds travel time where pyrophoric chemicals are used.

Fire Extinguishers –

An ABC dry powder extinguisher is appropriate for some of these reagents; however, Class D fire extinguishing materials may be required. Refer to the SDS for guidance on choice of extinguishing material. Extinguishing 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 material.
- Fire extinguisher training is required before working with pyrophoric chemicals.

Eye protection –

- Chemical Splash goggles or safety glasses (with side shields) that meet the ANSI Z.87.1 1989 standard must be worn whenever handling pyrophoric chemicals. Ordinary prescription glasses will NOT provide adequate protection unless they also meet this standard and have side shields. When there is the potential for splashes, goggles must be worn. When appropriate, a face shield should be worn in addition to eye protection.
- 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 that pose these risks should occur in a fume hood with the sash in the lowest feasible position. Portable safety shields, which provide protection to all laboratory occupants, are also encouraged.

Skin protection –

- Gloves must be worn when handling pyrophoric and water-reactive chemicals. Nitrile gloves are adequate for handling small quantities. However, nitrile gloves are combustible, and heavy chemical-resistant gloves may be appropriate for working with large quantities. Review the SDS and contact the Office of Laboratory and Field Safety 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. FR/CP lab coats are available through the Office of Laboratory and Field Safety lab coat program. Clothing, shirt and pants, should be cotton or wool. Synthetic clothing is strongly discouraged in laboratories where pyrophoric or water-reactive 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 using pyrophoric agents.

- We highly recommend that the lab coat and gloves be made out of Nomex material. Examples include the following:
    - Fisher Scientific cat. # 19-166-1070 Apparel, Bulwark™ Nomex™ IIIA HRC1 Lab Coat
    - Fisher Scientific cat. # 19-816-628 Gloves, Nomex, fire resistant

Emergency Procedures

Spills - Exert extreme caution due to potential spontaneous combustion and potential ignition of flammable solvents or other materials in the area. If the spill in unmanageable, call CMU police by dialing 911.

Appropriate spill media should be used to completely smother and cover any spills that occur. Do not use combustible materials (paper towels) to clean up a spill, as these may increase the risk of igniting the reactive compound. Follow the SOP procedure for cleanup.

Anyone exposed or on fire, immediately go to the nearest emergency shower and rinse for 15 minutes, removing all articles of clothing to ensure contaminant is completely removed. Call for assistance.

Fire - Evacuate laboratory and call CMU police by dialing 911. Do not use water to extinguish a pyrophoric or water-reactive fire. Refer to the SOP for proper extinguishing media.

Consult the CMU Chemical Hygiene Plan, Section IX "CHEMICAL EMERGENCY ACTION" section of the Office of Laboratory and Field Safety web site for more information.

Storage

- Store reactive materials as recommended in the safety data sheets (SDSs).
- Pyrophoric and water-reactive chemicals should be stored under an inert atmosphere or under kerosene as appropriate. Do not store with flammable materials or flammable liquids.
- Pyrophoric liquids, or compounds dissolved in a liquid, should be stored in sealed containers with PTFE-lined septa to prevent air exposure.
- Do not store in areas with heat/flames, oxidizers or water sources.
- Store pyrophoric and water-reactive materials in a watertight secondary container or a desiccator.
- Containers with pyrophoric or water-reactive chemicals should be clearly labeled with correct chemical names and hazards. Be sure the storage area is clearly labeled "Pyrophoric or Water-Reactive Chemicals".
- Ensure that sufficient protective solvent, oil, kerosene, or inert gas remains in the container while the material is stored. Do not let pyrophoric chemicals that are stored in solvents dry out. Check solvent levels periodically.

- Best practices dictate storing pyrophoric materials inside an inert atmosphere glove

box.

- Store the minimal amounts of pyrophoric materials as dictated by research. Do not stockpile pyrophoric materials in solvents as the solvents tend to evaporate over time changing the concentration of the solutions.
- Never return excess chemical to the original container. Small amounts of impurities introduced into the container may cause a fire or explosion.

Disposal

- Small amounts of unused or unwanted pyrophoric materials must be destroyed by careful quenching of the residue. Refer to the laboratory-specific hazardous material SOP. Proper disposal must be researched thoroughly and included in the SOP prior to the use of pyrophoric materials. Dispose of as hazardous waste.
- Do not leave containers with residues of pyrophoric materials open to the atmosphere due to uncontrolled ignition.

Consult the chemical SDS for proper disposal methods.

Contact the Hazardous Waste Manager before disposing of pyrophoric materials. (774-2770)

Appendix A: List of Pyrophoric Chemicals

(From the University of Minnesota)

Liquids:

Alkylaluminum reagents (Neat or in hydrocarbon solvents) (Neat reagents are VERY pyrophoric)
Alkyllithium reagents (Typically in hydrocarbon solvents) (Tert-butyllithium is VERY pyrophoric)
Alkenyllithium and Aryllithium reagents (Typically in hydrocarbon solvents)
Alkynyllithium reagents (Typically in hydrocarbon solvents)
Alkylzinc reagents (Neat reagents are pyrophoric)
Boranes (Neat reagents are pyrophoric)
Grignard Reagents (RMgX) (Typically in hydrocarbon solvents)
Partially or fully alkylated derivatives of metal and nonmetal hydrides (diethylaluminum hydride, diisobutylaluminum hydride, dichloromethylsilane) (Usually in liquid form or in solution.)
Alkylated metals (butyllithium, triethylboron, trimethylaluminum) (Usually in liquid form or in solution.)
Non-metal alkyls: R_3B, R_3P, R_3As; tetramethylsilane, tributylphosphine
Metal alkyls and aryls, such as, RLi, RNa, R_3Al, R_2Zn

Solids:

Alkali metals (lithium, sodium, potassium, especially sodium potassium alloy – NaK, and even more dangerous are cesium and rubidium)
Alkylated metal alkoxides or halides (dimethylaluminum chloride, diethylethoxyaluminum)
Finely divided metals (aluminum, bismuth, calcium, cobalt, hafnium, iron, magnesium, manganese, titanium, tin, uranium, zirconium)
Low valent metals (titanium dichloride)
Metal hydrides (potassium hydride, sodium hydride, lithium aluminum hydride, uranium trihydride)
Nonmetals (white phosphorous)
Metal carbonyls (dicobalt octacarbonyl, nickel carbonyl, iron (0) pentacarbonyl)
Used hydrogenation catalysts, e.g. Raney Nickel, 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, potassium sulfide, Aluminum phosphide

Gases:

Nonmetal hydrides (arsine, boranes, germane, phosphine, silane) (Most of these are actually gases.)

For an extensive list, see the University of Minnesota Department of Environmental Health and Safety, "Chemical and other Substances", Pyrophoric Materials Guidance Appendix: List of Pyrophoric Materials.

Recently used pyrophorics at CMU include:

- Butyllithium
- Methyllithium
- Phenylethynylmagnesium bromide
- Benzylmagnesium chloride solution, 1.0M in diethyl ether
- Trimethylaluminum solution in toluene
- Borane tetrahydrofuran complex solution, 1.0 M in THF
- Chlorotrimethylsilane
- Potassium metal
- Sodium metal

References:

1. *Guidance for Hazard Determination for Compliance with the OSHA Hazard Communication Standard (29 CFR 1910.1200)*, Edwin G. Foulke, Jr. (Assistant Secretary of Labor for Occupational Safety and Health), United States Department of Labor, Occupational Safety & Health Administration. http://www.osha.gov/dsg/hazcom/ghd053107.html

2. *Right to Know Hazard Communication Compliance Guide (SP-22)*, Michigan Occupational Safety and Health Administration, https://www.michigan.gov/leo/0,5863,7-336-94422_11407_30453-93831--,00.html#rtk

3. *Handling Pyrophoric Reagents*, Aldrich Chemical Company, Milwaukee, WI, Revised June 1995. http://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/Aldrich/Bulletin/al_techbull_al164.pdf

4. Pyrophoric Handling Policy, Carnegie Mellon University, Environmental Health and Safety, Pittsburg, PA,October 2019. https://www.cmu.edu/ehs/Guidelines/pyrophorichandlingprocedure.pdf

5. Techniques for Handling Pyrophoric Chemicals Video: https://www.youtube.com/watch?v=iLMl10X0Naw

6. *Tufts University Standard Operating Procedures(SOP) for Pyrophoric Chemicals*, Tufts University, Boston, MA. https://tufts.app.box.com/s/irhkiq88c605s40w8gesyqgzoryw3spz

8. University of Minnesota-Pyrophoric Chemical Guide, University of Minnesota, Twin Cities Campus, June 14, 2010. http://www.dehs.umn.edu/ressafety_hsr_cos.htm http://www.dehs.umn.edu/PDFs/Pyrophoric_Chemicals_Guide.pdf http://www.dehs.umn.edu/PDFs/PyrophoricMaterialsListAppendix.pdf

9. "Safe Operating Procedure Pyrophoric & Substances that emit flammable gases when contact with water. Hazards & Risk Minimization", University of Nebraska, Lincoln, NE, January 2013 http://ehs.unl.edu/sop/s-pyrophoric_%26_substances.pdf