Environmental Health & Safety Policy Manual		
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Safe Use and Storage of Pyrophoric and Water-Reactive Chemicals		

1.0 PURPOSE

This policy establishes general requirements for the safe storage, emergency response, inventory, and handling of pyrophoric and water-reactive chemicals. This document, in conjunction with the chemical's Safety Data Sheet (SDS), shall be used in the development of lab-specific Standard Operating Procedures for pyrophoric and water-reactive chemicals.

2.0 SCOPE

This policy applies to all personnel who handle, transfer, or store pyrophoric and water-reactive chemicals.

The primary hazard associated with pyrophoric chemicals is their ability to spontaneously ignite. Many pyrophoric chemicals are also water-reactive. Water-reactive chemicals may react violently with water or moisture in the air to produce a flammable or toxic gas. In routine lab use, the frequent combination of pyrophoric or water-reactive chemicals with flammable solvents increases the risk of fire hazard. These compounds require documented specialized training before use.

Other common hazards of pyrophoric and water-reactive chemicals may include corrosivity, teratogenicity, peroxide formation, and acute or chronic toxicity (may cause damage to the liver, kidneys, and central nervous system).

Failure to follow proper handling procedures can result in fire or explosion with the potential to cause significant damage to facilities, serious injuries, and death. Accordingly, the Supervisor/Principal Investigator will ensure a comprehensive lab-specific Standard Operating Procedure (SOP) is developed for any pyrophoric or water-reactive chemicals in use.

3.0 RESPONSIBILITIES

- The Environmental Health and Safety Department (EHS) shall assist supervisors and Principal Investigators in the development of lab-specific SOPs for pyrophoric and water-reactive chemicals.
- Supervisors/Principal Investigator (PI) shall:
  - Develop an SOP for all pyrophoric and water-reactive chemicals in use. This SOP shall address safe handling, storage, fire prevention and control, and spill clean-up procedures.
  - Ensure lab personnel receive documented training on the SOP(s) before beginning work with the chemical.
  - Ensure a safety shower and eyewash station is available within 10 seconds travel time from where pyrophoric or water-reactive chemicals are used.

  - Ensure only the smallest, practical amount of pyrophoric or water reactive chemicals are present in the lab.
- Laboratory personnel shall:
  - Work with pyrophoric or water-reactive chemicals only after gaining a full understanding of the SOP.
  - Wear appropriate Personal Protective Equipment (PPE) and ensure any directed administrative or engineering controls are followed.
  - Never work alone while handling pyrophoric or water-reactive chemicals.
  - Know the location of and how to operate a safety shower and eyewash station.

4.0 DEFINITIONS

- **Pyrophoric Material**
  OSHA 1910.1200 defines a pyrophoric material as a liquid, solid, or gas that will ignite spontaneously in air at a temperature of 130 degrees F (54.4 degrees C) or below. Pyrophoric chemicals can be grouped into liquids, solids and gases. Any form can ignite spontaneously when exposed to air (within five minutes or less). The Globally Harmonized System (GHS) uses Hazard Code H250 (catches fire spontaneously if exposed to air) to identify pyrophoric materials.
- **Water-Reactive Material**
  OSHA 1910.1200 defines water-reactive material as a chemical that reacts with water to release a gas that is either flammable or presents a health hazard. Water-reactive materials that produce a flammable gas are identified by GHS Hazard Code H260 (in contact with water releases flammable gases which may ignite spontaneously) or H261 (in contact with water releases flammable gas).

The GHS pictograms for H250, H260, and H261 are provided in Appendix A.

A limited list of pyrophoric chemicals is provided in Appendix B. For a detailed list of pyrophoric and water-reactive chemicals (not all inclusive), refer to Bretherick's Handbook of Reactive Chemical Hazards Sixth Edition Volume 1.

5.0 CONTROLLING HAZARDS

Handling of pyrophoric and water-reactive chemicals are typically high risk activities and must be controlled with adequate administrative and engineering controls, and the use of the proper Personal Protective Equipment.

Administrative Controls

Administrative controls include written procedures, chemical-specific SDS, technical bulletins, employee training, establishing designated or restricted areas, chemical procurement procedures, and preventive maintenance.

- Supervisors/PIs shall develop a lab-specific SOP for all pyrophoric and water-reactive reagents. These SOPs shall address safe handling, storage, fire prevention and control, and spill clean-up procedures. All lab personnel will receive documented training on the SOP(s) before beginning work with the chemical. See the Laboratory-Specific Training Checklist for more information.
- Trained lab personnel must never work alone when handling pyrophoric or water-reactive chemicals.

- To assist in the development of SOPs, see the Sigma-Aldrich Technical Bulletins Handling Pyrophoric Reagents (AL-164), Handling of Air-Sensitive Reagents (AL-134) and The Aldrich Sure/Pac™ System (AL-136), which provide guidance on the safe handling and transfer of air-sensitive and pyrophoric liquids.

Engineering Controls

Engineering controls are the most effective means of controlling hazards because they enclose the hazard or physically separate it from the lab worker. Examples include local exhaust ventilation systems, laboratory fume hoods, enclosures, and shields. Contact EHS for guidance on appropriate controls.

- **Glove (Dry) Box**
  Glove boxes offer the most secure and precise work area, and thus are the preferred engineering control for the regular handling pyrophoric chemicals. Pyrophoric and water-reactive chemicals that require inert or dry atmospheres must be handled within a glove box. Anyone working in a glove box must be trained and review the glove box SOP with their PI prior to beginning work.
- **Fume Hood**
  A chemical fume hood with exhaust ventilation is required when working with water-reactive chemicals to prevent buildup of toxic and flammable gases. Some pyrophoric chemicals are stored as flammable solvents and the use of a fume hood is required to prevent the release of flammable vapors into the laboratory. Work with the sash in the lowest possible position.
- **Safety Shields**
  Safety shields must be used for protection against possible explosions or uncontrolled reactions. Laboratory equipment must be shielded on all sides to ensure there is no line-of-sight exposure to personnel. The lab-specific SOP will specify whether a blast shield is required.

Personal Protective Equipment (PPE)

Protective clothing and equipment is not a substitute for adequate engineering controls. PPE must be selected on the basis of the hazards present, the type of materials used, and the manner in which they will be handled. To be effective, employees must understand the proper selection, use, and limitations of PPE. Users of pyrophoric chemicals must always consult with their PI and lab-specific SOP to determine task appropriate PPE before carrying out any procedures.

- **Eye Protection**
  - Chemical splash goggles or safety glasses that meet the ANSI Z.87.1 standard 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 possible position. Portable shields, which provide protection to all laboratory occupants, should also be used as necessary.

- **Skin Protection**
  - Non-synthetic clothing must be worn when working with pyrophoric chemicals. Clothing, shirt and pants, should be cotton or wool.
  - Always wear a NFPA 2112 compliant flame-resistant lab coat. Lab coats need to be buttoned and fit properly to cover as much skin as possible.
  - Appropriate shoes that cover the entire foot must be worn in all laboratories.
  - Gloves must be selected on the basis of their chemical resistance to the material(s) being handled, their suitability for the procedures being conducted, and their resistance to wear as well as temperature extremes.
  - For work involving large volumes of pyrophoric chemicals, a glove made of flame retardant materials is required in addition to a chemical-resistant, non-combustible glove. A chemical-resistant apron worn over the lab coat is also required.

For more information about general PPE requirements, refer to EHS-400.03, Personal Protective Equipment.

6.0 EMERGENCY PROCEDURES

The lab-specific SOP must include procedures that thoroughly address response actions to fires, explosions, spills, and injury to lab personnel. All lab personnel must be adequately trained in emergency response procedures before they begin work with a pyrophoric or water-reactive chemical. If you require assistance in the event of an emergency in the lab, contact University Police at 568-8999.

To assist in the development of lab-specific emergency response plans, refer to the U.S. Department of Energy's Handbook: Primer on Spontaneous Heating and Pyrophoricity for guidance on suitable fire extinguishing agents and safety precautions for specific chemicals.

The following provides general guidance on personal decontamination, spill response, and response to a fire. As noted above, if you require external support, always contact University Police. University Police will then contact Environmental Health and Safety and/or the Fire Department.

Once the emergency is addressed and you return to normal operations, ensure the incident is documented in accordance with EHS-400.06, Incident and Accident Reporting and Investigation Policy.

Personal Contamination

Consult the chemical-specific SDS for special first aid procedures. General first aid procedures for hazardous chemicals are provided below.

- **If inhaled -** Move to fresh air. Have victim rest in half-upright position. If you have training, perform artificial respiration if the victim is not breathing. Get medical attention immediately.
- **In case of skin contact -** Go to the nearest emergency shower if contaminated or on fire. A safety drench shower will be available within 10 seconds travel time where pyrophoric chemicals are used. Lab personnel must know the locations of the eyewashes and safety showers and how to activate them in an emergency.

Immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention immediately

- **In case of eye contact -** Check for and remove any contact lenses. Immediately flush eyes with plenty of water from emergency eyewash station for at least 15 minutes. Get medical attention immediately.

In the event of personal contamination requiring medical assistance, contact University Police at 568-8999 and communicate the following:

- Location of exposure
- Type of chemical involved
- Injuries involved
- Your location and contact information (or who to contact for further information)
- If possible, provide emergency responders with the chemical-specific SDS.

Spills

General procedures for chemical spills are addressed in EHS-200.02, Chemical Spill Response Policy and Procedures. However, you must consult the chemical-specific SDS to determine the appropriate spill response. Anticipate emergency situations and have proper handling equipment readily available for spills. Prior to beginning work, you must review the lab-specific SOP and chemical-specific SDS to determine the appropriate unreactive solvent needed to quench (neutralize/deactivate) the chemical. Do not attempt to handle a spill in which you are not trained or equipped for. General guidance for spill clean-up follows:

Simple Spill

A simple spill is generally one that does not spread rapidly and does not endanger people or property (except by direct contact). Simple spills can be cleaned up without assistance from outside the laboratory and should be managed by the user of the chemical. If you have training, you may cleanup simple spills using the methods described in the lab-specific SOP in addition to the general spill response guidance below.

Important factors that help you to determine whether you have a simple spill are:

- Amount of chemical spilled
- Specific chemical spilled
- Hazardous characteristics of chemical
- Location of chemical spilled

Risks are reduced by using small amounts of pyrophoric or water-reactive chemicals. A spill may not necessarily result in an immediate fire, but you must act quickly to disperse and neutralize the material to prevent this from happening. Some general guidance for spill response is as follows:

- **Pyrophoric chemicals:**
  - Assess the extent of danger.
  - DO NOT put water or flammable materials on spill.
  - If it is safe to do so, confine the spill to a small area using a spill kit or absorbent material.

  - Quench using the appropriate procedures.
- **Water-Reactive chemicals:**
  - Exert extreme caution due to potential spontaneous combustion and potential ignition of flammable solvents or other materials in the area.
  - DO NOT put water or flammable materials on spill.
  - For solid water-reactive chemical spills, cover with soda ash, shovel into a dry metal container, and cover again with soda ash.
  - Quench using the appropriate procedures.

Complicated Spill

Spills should be treated as a complicated spill if the result might be a fire that can't be safely extinguished by laboratory personnel, an explosion, or is a situation immediately dangerous to life and health. If you have any doubts about whether a spill can be classified as "simple", initiate the lab-specific emergency response plan and:

- Turn off ignition sources.
- Alert all personnel in the area.
- Evacuate the area.
- Activate the nearest fire alarm pull station.
- Close the door, but do not lock the door as you exit the lab.
- Immediately call for emergency assistance and communicate the following:
  - Location of spill/incident
  - Type of chemical involved and quantity spilled
  - Your location/contact information (or who to contact for further information)

Fire Control Measures

Consult the chemical-specific SDS to determine the appropriate fire extinguishing method. Anyone involved in handling pyrophoric or water-reactive chemicals must be trained on the selection and use of the appropriate extinguishers and aware of their locations. These extinguishers must be available within 10 seconds travel time from where chemicals are being handled.

Persons involved with a fire involving any pyrophoric or water-reactive chemical must evaluate the potential danger to themselves and others before attempting any action. Extinguish fires only if you can do so safely and quickly. Lab personnel must know the hazard characteristics of the specific chemical being handled in order to determine when and if a fire can be extinguished safely using the appropriate method. In the event of a fire, in addition to general guidance below, follow the fire control protocol detailed in the lab-specific SOP. The following is general fire control guidance:

- **Pyrophoric chemicals:**
  - A small beaker of dry sand or soda ash (sodium carbonate) in the work area is useful to extinguish any small fire that occurs at the syringe tip and to receive any last drops of reagent from the syringe.
  - The recommended fire extinguisher is a standard dry powder (ABC) type (e.g., dry sand, soda ash, calcium oxide (lime)) and should be within immediate reach in the event of an incident.
  - Dry sand or soda ash may cover and contain any small spill or fire that occurs.

  - Class D extinguishers are recommended for combustible solid metal fires (e.g., sodium), but not for organolithium reagents. Contact EHS if you need a Class D fire extinguisher.
  - DO NOT use a carbon dioxide fire extinguisher or water to attempt to extinguish a pyrophoric material fire as these types of extinguishers can actually enhance the combustion of some pyrophoric materials.
  - DO NOT use water on a pyrophoric reagent fire, as it can make the incident even worse.
  - DO NOT use combustible materials like paper towels to clean up a spill, as these materials may increase the risk of ignition with a pyrophoric chemical.
- **Water-Reactive chemicals:**
  - DO NOT use water in an attempt to extinguish a reactive material fire as it may enhance combustion.
  - The recommended fire extinguisher is a standard dry powder (ABC) type (e.g., dry sand, soda ash, calcium oxide (lime)) and should be within immediate reach in the event of an incident.
  - Class D extinguishers are recommended for combustible solid metal fires (e.g., sodium, potassium, lithium aluminum hydride).

If you have any doubts that you will be able to quickly extinguish the fire safely and successfully, then do not fight the fire and instead initiate the lab-specific emergency fire-response plan and:

- If anyone is exposed, or on fire, wash with copious amounts of water at the nearest emergency shower.
- Turn off all ignition sources if this can be done safely.
- Alert all personnel in the area.
- Evacuate the area.
- Activate the nearest fire alarm pull station.
- Close the door, but do not lock door as you exit the lab.
- Immediately call for emergency assistance and communicate the following:
  - Location of fire
  - Type of chemical involved
  - Any injuries involved
  - Your location/contact information (or who to contact for further information)

7.0 ORDERING AND STORAGE

When ordering pyrophoric or water-reactive chemicals, order only what is needed. Check inventory regularly and dispose of outdated or unnecessary chemicals. For more information refer to EHS-200.05, Chemical Ordering and Storage Procedures.

Store reactive materials as required in the chemical-specific SDS. 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.

Never return excess chemicals to the original container. Small amounts of impurities may be introduced into the container which may cause a fire or explosion.

The following are general guidelines that must be used in combination with chemical-specific storage recommendations described in the SDS.

Storing pyrophoric material:

- Pyrophoric reagents must be handled and stored in a manner to avoid exposure to atmospheric oxygen and moisture.
- Glove boxes are commonly suitable for storage location of pyrophoric chemicals (stored under inert gas).
- Store in a separate secondary container and away from incompatibilities.
- Do not store pyrophoric chemicals with flammable materials or in a flammable liquids storage cabinet.
- Containers carrying pyrophoric materials must be clearly labeled with the correct chemical name and hazard warning.
- If pyrophoric reagents are received in a specially designed shipping, storage or dispensing container, 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.
- For storage of excess chemicals, prepare an appropriate storage vessel in the following manner:
  - Dry the clean and empty storage container thoroughly.
  - Select a septum that fits snugly into the neck of the vessel.
  - Insert septum into neck in a way that prevents atmosphere from entering the clean, dry (or reagent filled) flask.
  - Insert a needle to inject inert gas and to maintain a blanket of dry, inert gas above the reactive reagent and quickly insert a second needle to vent the flask.
  - Once the vessel is fully purged with inert gas, remove the vent needle and add the reagent carefully, then remove the gas line.
- For long-term storage, the septum should be secured with a copper wire.

Storing water-reactive chemicals:

- Over time, pressure may increase causing containers to burst. Keep container tightly closed in a cool, dry, well-ventilated place and protected from sunlight.
- Keep in a dry place (such as a desiccator or a dry box or glove box) free of moisture/humidity.
- Never allow contact with water.
- Store and handle under inert gas (nitrogen, argon, etc.).
- Store away from heat sources and in a flame proof area.
- Store in a location separated from acids, oxidizing, and other incompatible materials.
- Store in a separate secondary container and label the material clearly.
- Hazard communication label on the container must read “Water-Reactive”.
- Do not leave the container near a lab sink, emergency eyewash or safety shower.
- Do not leave the container on the bench top unattended.

8.0 WASTE DISPOSAL

Correct disposal procedures for pyrophoric and water-reactive chemicals depend on the identity of the chemical and the condition of the container. Reactions must be carefully

and completely quenched as part of your experimental procedure before they are collected for waste disposal. In addition to the general practices described below, follow procedures established by the PI in the lab-specific SOP and chemical-specific SDS.

Decontamination of Pyrophoric and Water-Reactive Chemicals
Quenching is the process of readying pyrophoric or water-reactive waste chemicals for disposal by neutralizing/deactivating the materials using unreactive solvents. Make sure that the pyrophoric or water-reactive residues in empty containers, spatulas, and other contaminated items are quenched before disposal.

- 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 solvent from first rinse 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 for at least a week.
- The empty container, solvent rinses, and water rinse should be disposed as hazardous waste by EHS staff and should not be mixed with incompatible waste streams.

General procedures for proper handling and disposal of hazardous chemical waste is detailed in EHS-200.04, Chemical Waste Management Procedures. To request a pickup of chemical waste, authorized personnel must use the Facility Services online service request work order system.

9.0 REFERENCES

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10.0 APPENDICES

A – GHS Classification and Labelling Summary for H250, H260, and H261

B – Carnegie Mellon List of Pyrophoric Materials (not all inclusive)

LSU Health NEW ORLEANS

GHS Classification and Labelling Summary for H250, H260, and H261

Category	Pictogram	Signal Word	Code: Hazard Statements
B.9 PYROPHORIC LIQUIDS			
1		DANGER	H250: Catches fire spontaneously if exposed to air
B.10 PYROPHORIC SOLIDS			
1		DANGER	H250: Catches fire spontaneously if exposed to air
B.12 CHEMICALS WHICH, IN CONTACT WITH WATER, EMITS A FLAMMABLE GAS			
1		DANGER	H260: In contact with water releases flammable gases which may ignite spontaneously
2		DANGER	H261: In contact with water releases flammable gas
3		WARNING	H261: In contact with water releases flammable gas

OSHA adopted GHS classification and labelling. Note: The statement codes are for reference purposes only.

Appendix A

LSU Health NEW ORLEANS

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

Appendix B