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ENVIRONMENTAL HEALTH AND SAFETY OFFICE**

**STANDARD OPERATING PROCEDURE
FOR PYROPHORIC MATERIALS**

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LIST OF ABBREVIATIONS AND ACRONYMS

EH&S	Environmental Health and Safety
HIM/NRB	Harvard Institutes of Medicine/New Research Building
MSDS	material safety data sheet
OSHA	U.S. Occupational Health and Safety Administration
PPE	personal protective equipment
SOP	standard operating procedure
°F	degrees Fahrenheit

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1.0 INTRODUCTION

It is the policy of the Harvard Institutes of Medicine and New Research Building (HIM/NRB) to provide a safe and healthy workplace in compliance with the Occupational Safety and Health Act of 1970 and with regulations of the U.S. Department of Labor. The full U.S. Occupational Safety and Health Administration (OSHA) standard can be found at: <http://www.osha.gov/comp-links.html>.

This standard operating procedure (SOP) will review methods for working safely with pyrophoric materials. It will describe pyrophoric substances characteristics, engineering controls/ventilation, personal protective equipment, emergency response, and their disposal at the HIM/NRB facility.

Pyrophorics are defined as chemicals that may spontaneously ignite in dry or moist air below 130 degrees Fahrenheit (°F).¹ Many pyrophoric materials are also water reactive, reacting vigorously with water or high humidity, often igniting upon contact. Some chemicals that may be pyrophoric are:

- Alkali metals
- Grignard reagents
- Finely divided metals
- Metal carbonyls
- Titanium dichloride
- White phosphorus
- Tert-butyllithium

Typically, pyrophoric materials are manipulated in an inert (unreactive) atmosphere of nitrogen or argon using specialized glassware. Refer to the Sections 4.0 and 6.0 for details.

¹ http://www2.iccsafe.org/states/seattle/seattle_fire/PDFs/Chapter%2041.pdf

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2.0 TRAINING REQUIREMENTS

These highly reactive substances are quite useful in the synthesis of organic chemicals, but special training is required to store and handle these materials safely. Only qualified and trained individuals may use pyrophoric materials in the HIM/NRB.

Principal Investigators must ensure researcher's have job-specific training for handling pyrophorics. In addition, the laboratory manager must read this SOP so s/he understands the hazards associated with working with these types of materials. The HIM/NRB Environmental Health and Safety (EH&S) Office requires written training records for laboratory members, who are trained to use pyrophorics. This training will include reviews of the following:

- This SOP.
- The corresponding material safety data sheet (MSDS) for the pyrophoric material(s).
- The handling sheet for the pyrophoric material(s), if applicable.
- Sigma-Aldrich Technical Bulletin numbers 134 and 164. They are available on the following link: <http://www.sigmaaldrich.com/chemistry/aldrich-chemistry/tech-bulletins/tech-bulletin-numbers.html>.

A quiz will be administered to the researcher (does not include undergraduate student, since they should be supervised by a experience researcher or user at all times) to document that the researcher understands the hazards, properties, and proper techniques associated with working with the pyrophoric material. The researcher must receive a 100% to pass the quiz. A researcher will be unable to work with the pyrophoric material until s/he receives 100% on the quiz. The quiz is available from and will be graded by the HIM/NRB EH&S Office. A copy of the training record will be provided to the HIM/NRB EH&S Office for their records.

An experienced researcher trained in the above protocols must document that the new trainee has observed the pyrophoric chemical's usage by another experienced and trained individual and performed the procedure under the experienced user's supervision.

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The “experienced user” is a user that has documented experience and education that is appropriate to be the representative of the laboratory responsible for the training of fellow employees. This user must be responsible and knowledgeable; s/he is the laboratory member responsible for answering questions about pyrophoric materials. In many cases, this person will be the principal investigator of the laboratory but it may also be a representative designated by the principal investigator. The HIM/NRB EH&S Office will review the “experienced user’s” qualifications and validate in the training records that s/he has reviewed the training process with trainees and that trainees appear competent to work with pyrophoric materials.

3.0 PYROPHORIC CHEMICAL CHARACTERISTICS

The following are some of the characteristics associated with pyrophoric materials. The chemical characteristics of pyrophoric materials vary from material to material. As a result, it is important that researchers review the MSDS associated with the pyrophoric material, as outlined in Section 2.0.

- May spontaneously ignite in the air at room temperature.
- May react with moisture or oxygen in the air.
- Should never be exposed to the atmosphere.
- Are either organometallic compounds or alkali metals.
- Tend to be associated with flammable solvents.

Other hazards include corrosivity, water reactivity, peroxide formation, and/or toxicity.

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4.0 STORAGE REQUIREMENTS

Pyrophoric materials must be stored very carefully, often under an inert gas (i.e., nitrogen, argon) to keep them from exposure to air or moisture. Some materials are included in this group of hazards because they will spark with only a little friction.

Avoid storage areas with heat/flames, oxidizers, and water sources. As a result, it is important to store pyrophoric materials in accordance with their MSDS and to keep the quantities to a minimum.

4.1 SOLIDS

Many pyrophoric solids are sold as solutions, or dispersions in mineral oil or are covered with hydrocarbon solvents to facilitate use. It is important to avoid prolonged exposure of pyrophoric solids to air.

Pyrophoric solids should be stored in a designated glove box, closed system, or a location that meets the manufacture requirements.

4.2 LIQUIDS

The HIM/NRB EH&S Office recommends that pyrophoric liquids be purchased in a Sure/Seal™ bottle, which incorporates the inert composition of amber glass bottles with a time-tested crimp-top system. This design ensures the exceptional state of dryness achieved at time of purification is maintained throughout long-term storage and use. Before filling, low level traces of moisture are removed from the bottle through oven drying. The bottles are then filled under an inert atmosphere of dry nitrogen to prevent moisture build-up and sealed with a unique Sure/Seal liner and crown cap.² Large quantities of volume (>100 milliliters) and/or a different type of seal should be reported to the HIM/NRB EH&S Office for review prior to ordering the material.

² Sigma-Aldrich®, Sure/Seal™ Bottles, accessed April 21, 2009.
<http://www.sigmaaldrich.com/chemistry/solvents/products.html?TablePage=14577656>

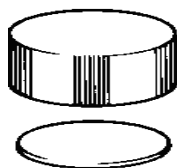
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Pyrophoric liquids should be stored in a vessel containing an inert atmosphere and in a portion of the laboratory designated for pyrophoric storage.

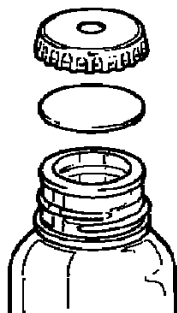
4.3 RESTRICTIONS

Due to various storage factors, it is up to the laboratory group's professional judgment to determine a safe storage time length of a particular pyrophoric after opening (case by case basis). The seal and the general condition of the pyrophoric container must be visually checked for integrity on a regular basis, any sign of deterioration of the seal or the general condition of the pyrophoric container, the pyrophoric must be disposed of as soon as possible. As a general precaution, after opening pyrophorics may only be kept up to one year maximum before being disposed of as hazardous waste. During storage a "Bakelite" cap should be kept on the bottle to keep air from the chemical. The Sigma Sure/Seal system is a patented technology that has a neck with glass crown and threads sealed by a Teflon laced liner, metal crown cap with a 1/4" hole, natural rubber liner, and finally, a Bakelite cap that seals all of the components. This can be seen in the following drawing.

Bakelite Cap with Natural Rubber Liner



Metal Crown Cap with Teflon faced liner



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When working with a pyrophoric material the Bakelite cap and its associated rubber liner are removed. A needle can then be placed through the metal crown cap and Teflon laced liner into the material. The Teflon laced liner will reseal once the needle is removed. To ensure that the resealing is complete the Bakelite cap is replaced and the Teflon laced liner will reseal completely against the metal crown cap.

Used pyrophoric material must never be returned to the pyrophoric chemical's stock solution. Prior to completing an experiment all used pyrophoric material that is on associated equipment must be neutralized or safely transferred to hazardous waste containers; do not leave these containers until they are confirmed to be safe and stable. Neutralization and disposal of stock solutions of pyrophorics will be conducted by the licensed HIM/NRB hazardous waste vendor.

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5.0 HAZARD COMMUNICATION

Under the OSHA Hazard Communication Standard Title 29 Code of Federal Regulations Part 1910.1200, containers of hazardous materials must be labeled with the full name of the chemical (no abbreviations) and the hazard associated with the chemical.

The hazards associated with pyrophorics are such that all containers must be labeled with the full chemical name and the hazard(s) associated with the material (i.e., pyrophoric, flammable, corrosive, toxic, water reactive).

In addition, the designated chemical fume hood, glove box, closed system, or a location that meets the manufacture requirements used to store the pyrophoric materials must be labeled with the chemical name and the hazard(s) associated with the material. Refer to Figure 1 for an example.

<p>Chemical Name: tert-Butyllithium in Pentane Hazards: Flammable, Toxic, Corrosive, Water Reactive, Pyrophoric</p>

Figure 1 Hazard Communication Label

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6.0 HANDLING AND ENGINEERING CONTROLS

Due to the hazards associated with pyrophoric materials, the following steps **MUST** be followed before/while working with such materials:

- The laboratory must obtain the appropriate personal protective equipment (PPE) (gloves, fire resistant laboratory coat, safety goggles) for the experiment. Refer to Section 7.0 for specific details.
- Ensure the engineering controls and waste storage containers are available for the experiment. Chemical fume hoods must be certified to ensure adequate ventilation during the experiment.
- **NEVER WORK ALONE WITH PYROPHORIC MATERIALS.**
- New users of pyrophoric reagents must work under the close supervision of an experienced user. Before a researcher can work without an experienced user present, they need to conduct the procedure without help but under the supervision of the trainer and a member of the HIM/NRB EH&S Office.
- People using pyrophoric materials must have a copy of this SOP and the MSDS with them while they are using the pyrophoric materials to ensure proper procedures when working these hazardous chemicals.
- Remove all unused equipment and flammable materials from the area (including hazardous waste containers).
- All work with pyrophoric solids must be performed in a designated glove box, closed system, or a location that meets the manufacturer's requirements. Ensure the designated glove box has the Hazard Communication label, which is provided in Section 5.0.

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- All equipment utilizing pyrophoric materials must be setup in a designated chemical fume hood. Ensure the designated chemical fume hood has the Hazard Communication label, which is provided in Section 5.0.
- The designated chemical fume hood's sash must be used at or below 18" to prevent a splash hazard to the researcher.
- Other members of the laboratory and the laboratory manager must be informed where pyrophoric materials are used and stored as well as the duration of the experiment. Prior to an experiment with pyrophorics, HIM/NRB EH&S needs to be notified.
- Depending on the pyrophoric material, a Class B or Class D fire extinguisher is required. Additionally, powdered lime, if acceptable, should be present within arms reach of the pyrophoric material to completely smother and cover any minor spill that occurs.³ Refer to the MSDS prior to working with the chemical for details. Contact the Facility Manager to obtain the appropriate fire extinguisher.

³ *Handling Pyrophoric Reagents*, Technical Bulletin AL-164, revised 6/95.
http://www.sigmaaldrich.com/etc/medialib/docs/Aldrich/Bulletin/al_techbull_al164.Par.0001.File.tmp/al_techbull_al164.pdf.

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7.0 PERSONAL PROTECTIVE EQUIPMENT

Personal protective equipment (PPE) is required at all times when working with pyrophorics. HIM/NRB tenants must be trained in the proper use and limitations of the PPE they are using with respect to the pyrophorics.

7.1 EYE PROTECTION

Eye protection is required when working with pyrophorics. Chemical splash goggles and/or a face shield, which meet the American National Standards Institute (ANSI) Z87.1-2003 standard, must be worn when working with pyrophoric materials.

If there is a splash hazard, a face shield should be worn. A face shield is required when there is a risk of explosion, large splash hazard, or a highly exothermic reaction.⁴

7.2 HAND PROTECTION

Heavy chemical-resistant gloves must be worn while working with pyrophoric materials. For more information regarding the type of gloves, please contact the HIM/NRB EH&S Office.

7.3 BODY PROTECTION

A flame resistant laboratory coat (i.e., Nomex®, which is certified as a flammable resistant material) must be worn at all times. In addition, a flame resistant apron worn over the laboratory coat is required when working with large quantities.⁵

Individuals working with pyrophoric materials are required to wear pants or a long skirt to protect their legs. Shoes must be impervious or resistant to the agents used. Per laboratory rules no open toed shoes are permitted in a laboratory setting.

⁴ University of California at Los Angeles Chemistry & Biochemistry, *Procedures for Safe Use of Pyrophoric Solids*, 2/2009.

<http://www.chemistry.ucla.edu/file-storage/publicview/pdfs/ProceduresSafeSolids.pdf>

⁵ Ibid.

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8.0 EMERGENCY RESPONSE

In the event of an emergency involving pyrophorics:

- HIM/NRB tenants should follow the procedures outlined in the HIM/NRB Emergency Action Plan and provided in the manufacturer's MSDS.
- The researchers should be familiar with the MSDS PRIOR to any emergency. Researchers must also be familiar with where the nearest emergency equipment is located in their work area. Be sure appropriate fire extinguishing materials are present prior to work.
- If pyrophorics are spilled in the laboratory the researcher must use powdered lime (calcium oxide [CaO]), a fire extinguisher (if appropriate), or another appropriate agent to smother the material prior to cleaning it up. The lime should be within arms reach during all work with pyrophorics, if appropriate.⁶
- All researchers using pyrophorics should be prepared to clean up a pyrophoric spill prior to beginning work (see Section 8.2 for spill response).

8.1 FIRST AID MEASURES

Typically, pyrophorics are **water reactive**; water should only be used on the area if it can be inundated to remove the chemical from the body. If inundation is impossible then it is best to smother the fire. After any fire has been neutralized the occupational health or emergency department of the individual's institution should be visited.

If ingested, obtain medical attention from the institution's occupational health department immediately.

In the event of inhalation, move the person to fresh air and seek medical attention at the institution's occupational health or department at once.

In an emergency situation, call 911 or go to the nearest emergency department.

⁶ *Handling Pyrophoric Reagents*, Technical Bulletin AL-164, revised 6/95.

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8.2 SPILL RESPONSE

In an event of a spill, close the chemical fume hood sash and evacuate the entire laboratory. Once at a safe location, call 911 then the Facilities Operation Center at 617-432-1901 to report the spill. A subcontractor will be responsible for cleaning up the spill and disposing of the hazardous waste associated with the spill.

8.2.1 Small Spill

In the event of a small spill of pyrophoric material the researcher should use lime and/or appropriate fire extinguisher (as applicable) to neutralize the chemical if they are comfortable and trained. The training must be documented per Section 2.0. The researcher should follow the MSDS recommendations in neutralizing the pyrophoric. The spill must be reported to Facilities at 617-432-1901.

8.2.2 Large Spill

In the event of a large spill (>100 ml) of pyrophoric material the researcher should evacuate the laboratory immediately. Pull the fire alarm if a fire has developed (or may), otherwise contact 617-432-1901 immediately. Call 911 immediately, if appropriate.

NOTE: Small and large size spills are not objectively defined within the above sections. Circumstances and personnel available to respond to a spill make such an objective determination difficult. A spill of any volume of pyrophoric agents near flammable materials would normally be handled under section 8.2.2—Large Spill. A spill of pyrophoric material that is contained within a laboratory fume hood without combustibles in the vicinity and with trained personnel and fire fighting supplies readily available may be handled under section 8.2.1—Small Spill. In any event the responders and condition of the spill will determine the appropriate response.

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9.0 PROPER DISPOSAL

Other hazards associated with pyrophorics are flammable, corrosive, toxic, water reactive toxic, flammable, and/or reactive. As a result, they need to be treated as hazardous waste.

When work with pyrophorics is complete, the associated waste must be in a container safe for the hazardous waste contractor to transport to the main accumulation area. The pyrophoric material's disposal as hazardous waste will be handled by the hazardous waste subcontractor.

In the laboratory, after using the material, it must be placed into a safe and compatible hazardous waste container; the container must be labeled with a hazardous waste tag containing the following information:

- Declare "Hazardous Waste"
- Contents listed with no abbreviations
- Applicable hazards checked off (ignitable, toxic)
- Dated only when full or if the laboratory personnel are no longer adding waste to the container
- Add "Pyrophoric" to label

Call the HIM/NRB EH&S Office at 617-432-6184 to have the hazardous waste subcontractor remove the container.