

PYROPHORIC MATERIALS PROGRAM - External

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INTRODUCTION

Pyrophoric materials are materials that will spontaneously ignite in air at room temperature. Use of pyrophoric materials requires special care from a health and safety standpoint, as well as a legal standpoint. This document outlines the requirements for pyrophoric material users, as well as EH&S in the administration of the pyrophoric materials program.

OBJECTIVES

The objectives of this program include, but are not limited to:

- Ensure that researchers working with pyrophoric materials are meeting the minimum safety requirements
- Assist the Fire Prevention Team with ensuring the campus meets all applicable fire codes

RESPONSIBILITIES

Environmental Health and Safety

EH&S is responsible for the management of the campus’ chemical inventory, including pyrophoric materials, and for the generation of reports based on the inventory data. EH&S works with laboratories to verify that all requirements of working with pyrophoric materials, as outlined by this pyrophoric materials program, are met.

Principal Investigators (PIs)

The PI is responsible for maintaining safety protocols in their laboratory spaces. This involves making sure their laboratory personnel are properly trained for hazards that may be present in the laboratory, and that training is documented. The PI is also responsible for making sure that

all safety precautions are being upheld in their laboratory space, including use of Standard Operating Procedures (SOPs) and adherence to the [Personal Protective Equipment \(PPE\) policy](#). The PI ensures that the inventory in their space is regularly managed, and annually certifies that their inventory in UC Chemicals is accurate. While a PI may delegate tasks related to safety to members of their laboratory, the ultimate responsibility of safety in the space remains with the PI.


Laboratory Personnel

Laboratory Personnel are individuals who work in the laboratory. Laboratory personnel are required to follow all safety protocols in the laboratory as outlined by the PI, including following SOPs and wearing required PPE. Any changes to established procedure or amounts should be approved by the PI before making the change.

RECOGNIZING PYROPHORIC MATERIAL

A pyrophoric material is defined as any material which will ignite within 5 minutes of coming into contact with air. Common pyrophoric chemicals include alkylated lithium compounds, such as n-butyllithium, and organometallics of main group metals, such as trimethylaluminum. Pyrophoric gases are less common, but include silane. The packaging and containers of pyrophoric materials will be labeled with the Flame GHS symbol, use the SDS will include the signal word “Danger,” and the hazard statement “H250 - Catches fire spontaneously if exposed to air.”

Figure 1: Example SDS Section 2, showing label elements used for pyrophoric materials

2. HAZARDS IDENTIFICATION	
2.1 Classification of the substance or mixture	
GHS Classification in accordance with 29 CFR 1910 (OSHA HCS)	
Flammable liquids (Category 2), H225	
Pyrophoric liquids (Category 1), H250	
Substances and mixtures, which in contact with water, emit flammable gases (Category 2), H261	
Skin corrosion (Category 1B), H314	
Serious eye damage (Category 1), H318	
Reproductive toxicity (Category 2), H361	
Specific target organ toxicity - single exposure (Category 3), Central nervous system, H336	
Specific target organ toxicity - repeated exposure, Inhalation (Category 2), H373	
Aspiration hazard (Category 1), H304	
Acute aquatic toxicity (Category 2), H401	
Chronic aquatic toxicity (Category 2), H411	
For the full text of the H-Statements mentioned in this Section, see Section 16.	
2.2 GHS Label elements, including precautionary statements	
Pictogram	
Signal word	Danger
Hazard statement(s)	
H225	Highly flammable liquid and vapour.
H250	Catches fire spontaneously if exposed to air.
H261	In contact with water releases flammable gases.
H304	May be fatal if swallowed and enters airways.
H314	Causes severe skin burns and eye damage.
H318	Causes serious eye damage.

BASIC REQUIREMENTS FOR USING PYROPHORIC MATERIALS IN A LAB

Because of the increased hazards in normal pyrophoric conditions, there are special requirements for use and storage of pyrophoric materials, including reporting requirements.

The basic requirements for using pyrophoric materials in a laboratory are as follows:

1. The laboratory space must meet the requirements for safe use and storage of pyrophoric material. Material must be used and stored in a fully sprinklered building, as approved by the Fire Marshal, and appropriate storage must be available and used.
2. Inventory is regularly managed, and annually certified, using the UC Chemicals program.
3. An approved SOP must be in place for using pyrophoric materials, signed by the PI and all users of pyrophoric materials in the lab.
4. Users of pyrophoric materials are required to take the [Flame Resistant Glove](#) training course in LMS
5. Users must request flame resistant gloves from EH&S.

Details about each requirement are given below. These requirements should be fulfilled, and verified by the campus Chemical Hygiene Officer, before pyrophoric materials are ordered and brought into the lab space.

LABORATORY SPACE REQUIREMENTS

There are minimum requirements for laboratory spaces using pyrophoric materials on campus, and not every space on campus is appropriate. The following conditions must be met in order for a laboratory space to be approved for pyrophoric use:

1. Material must be used in a fully sprinklered building, as approved by the Fire Marshal. The California Fire Code ([CA Fire Code Chapter 50 Section 5003 Table 5003.1.1\(1\)](#)) states that pyrophoric materials are “allowed only in buildings equipped throughout with an approved automatic sprinkler system.” To determine if the building you are working in is acceptable for using pyrophoric materials, please contact the Chemical Hygiene Officer at EH&S ehslaboratory@ucr.edu.
2. Pyrophoric material should be stored under an inert atmosphere.
 - a. Whenever possible, storage and use in a glove box is preferred.
 - b. If a glove box is not available, use should be in a fume hood under an inert atmosphere.
 - c. Pyrophoric gases have specific requirements above and beyond other hazardous gases, potentially including significant infrastructure investments. Please contact ehslaboratory@ucr.edu to discuss your pyrophoric gas plans before starting work.
3. If storage in a refrigerator or freezer is required, the refrigerator or freezer must be explosion proof and labeled.

INVENTORY MANAGEMENT

Inventory updates are the responsibility of the laboratory that purchases them. Having an updated inventory allows for accurate response in hazardous situations, particularly in spaces with pyrophoric materials. Since pyrophoric materials have stricter requirements for managing and reporting, adding pyrophoric chemicals as received, removing as disposed, and certifying the inventory annually allows us to comply with these requirements. To reduce risk, it is recommended to minimize ordering and keep only a few months stock of pyrophoric materials.

PYROPHORIC SOP

A generic SOP created by EH&S is available in Appendix A, which covers the basic safety requirements of handling pyrophoric liquids and solids in a laboratory setting. One requirement of the SOP is defining the largest allowed quantity without PI approval, to keep reaction size low. While it is understood that the requirements of a research laboratory may require varied and changing processes, it is strongly encouraged, whenever possible, to outline specific processes in detail when working with hazardous substances. SOP should be signed by the PI, along with anyone in the laboratory using or handling pyrophorics in any way.

FLAME RESISTANT GLOVES

Flame resistant glove training is available on the UC Learning Center, and required for any researchers working with pyrophoric materials. This short, 4-minute video gives an overview of using flame resistant gloves with pyrophoric liquids, including why they are used, and how to select the right inner and outer gloves. EH&S has a selection of Ansell flame resistant gloves available in sizes from small to extra-large. Make a PPE appointment at <https://ucrebs.simplybook.me/v2/> to come to EH&S and select the size of glove that works best for you.

EH&S VERIFICATION

When a laboratory is ready to start working with pyrophoric materials, contact the Chemical Hygiene Officer at ehslaboratory@ucr.edu with your building information, to first verify that the building the work is intended to be done in meets the Fire Marshal's requirements. Once determined that the building is appropriate, fill out the Pyrophoric Material Usage Form in Appendix B and send to EH&S at ehslaboratory@ucr.edu. Once received, the Chemical Hygiene Officer will schedule an appointment to visit the lab to verify. Once verified, the laboratory can start ordering and using pyrophoric materials. Continued meeting of the requirements for pyrophoric materials will be verified during annual scheduled laboratory evaluations.

Appendix A: Pyrophoric and Self-Heating Liquids and Solids SOP

This document covers basic chemical safety information for pyrophoric and self-heating liquids and solids. The use of any pyrophoric chemical is subject to pre-approval by the Principal Investigator (PI) and/or Supervisor. **DO NOT USE PYROPHORICS UNTIL YOU HAVE OBTAINED THE NECESSARY PRE-APPROVAL.**

Pyrophoric and Self-Heating Liquids and Solids

A pyrophoric material is defined by the National Fire Protection Agency (NFPA) as having an autoignition temperature below 130°F (55°C). A self-heating material is one which reacts with air, in the absence of external energy, to produce heat. Self-heating materials may ignite if stored in large quantities. These materials typically also react violently with water. Because of this, **pyrophoric and self-heating liquids and solids must always be handled under inert atmosphere.**



Personal Protective Equipment & Personnel Monitoring



Lab Coat

Flame resistant lab coat.



Gloves

If used outside of a glove box, fire-resistant hand protection (e.g. chloroprene gloves over flame-resistant glove liners).



Eye Protection

ANSI Z87.1-compliant safety glasses, or safety goggles if a splash hazard is present. Face shield is required any time there is a risk of explosion, large splash hazard or a highly exothermic reaction.



Face Shield

Labeling & Storage

- Store pyrophoric liquids and solids 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 labeled with the correct chemical name and hazard warning.

Cautions & Considerations

Use and store only in fully-sprinklered buildings. **Before** working with pyrophoric reagents, read the relevant Safety Data Sheets (SDS) and understand the hazards. The SDS must be reviewed before using an unfamiliar chemical and periodically as a reminder.

Engineering Controls, Equipment & Materials

Glove Box

Whenever possible, pyrophorics should be handled inside of a glove box.

Fume Hood

If a glove box is not possible, a Schlenk line inside of a fume hood may be used to provide an inert atmosphere for working with pyrophorics.

Housekeeping

Spills

If pyrophoric materials spill in a glove box, quench the spilled material slowly with isopropanol. Absorb with a non-combustible absorbent, and dispose as hazardous solid waste. Call 911 from a campus phone (or (951) 827-5222 from a cell phone) for emergency assistance if necessary.

Quenching

Do not return unused pyrophoric materials to their original container. Small amounts of unused pyrophoric materials can be quenched under inert atmosphere with adequate cooling by slowly adding first isopropanol, then methanol, then water.

Waste

Larger quantities of pyrophoric chemicals can be disposed of as hazardous waste. Use WASTE to schedule a pickup. Carefully package and label all wastes to alert the hazardous waste team of the specific hazard.

First Aid & Emergencies**Fire**

Call 911 from a campus phone (or (951) 827-5222 from a cell phone) for assistance with all fires, even if extinguished. If you are trained and feel comfortable to do so, extinguish the fire with a dry chemical fire extinguisher (classes ABC or D), CO₂ type extinguishers are **not** acceptable. **DO NOT** attempt to use water to put out a fire of this type.

Skin or Eye Contact

Remove contaminated clothing and accessories; flush affected area with water for a minimum of **15 minutes** in the safety shower or eyewash. If symptoms persist, get medical attention.

Detailed Protocol

[Insert or attach a copy of your specific laboratory procedures for this process, hazardous chemical, or hazard class. If laboratory procedures are subject to frequent change as in a basic research environment, the paragraphs below may be sufficient to define the process for this hazardous chemical]

All lab workers who will be using a pyrophoric solid must review this SOP and sign the associated training sheet. Lab workers must have specific training on the proper handling of and understand the hazards.

Lab workers using a pyrophoric solid must demonstrate competence to the Principal Investigator or designee by being able to 1) identify the hazards and list any particularly hazardous handling techniques (use of a Schlenk line, rotary evaporation, cannula transfer, extremes of pressure or temperature, etc.), 2) list the foreseeable emergency situations, 3) describe the proper response to the emergency situations, and 4) know the control measures to minimize the risks.

The research laboratory requires variation in reaction conditions to develop and optimize new chemical or biological transformations. The researcher must seek literature precedent for reaction conditions that have reasonable similarities to new chemistry that is planned with a pyrophoric solid described in this SOP. The researcher must also consult the PI or designated, experienced research coworker for approval to proceed with chemical or biological transformations that have little literature or local research group precedent. PI approval must also be obtained for significant scale-up of new chemistry or biological transformations.

When working in the lab, a laboratory worker must:

1. Not work alone
2. Be cognizant of all of the SDS and safety information presented in this document
3. Follow all related SOPs in the laboratory SOP bank (PPE, syringe techniques, waste disposal, etc. as appropriately modified by any specific information in the SDS information presented in this document)
4. Employ (< quantity) of this a pyrophoric liquid or solid in any given reaction (larger quantities **REQUIRE** the approval of PI or designee)
5. Discuss ALL issues or concerns regarding a pyrophoric solid with the PI prior to its use.

If there is an unusual or unexpected occurrence when using this material(s), the occurrence must be documented and discussed with the Principal Investigator or Lab Supervisor and others who might be using [chemical name]. Unusual or unexpected occurrences might include a fire, explosion, sudden rise or drop in temperature, increased rate of gas evolution, color change, phase change, or separation into layers.

Appendix B: Pyrophoric Material Use Request Form

Before ordering and using pyrophoric materials in a laboratory, complete and submit to EH&S at ehslaboratory@ucr.edu. The Chemical Hygiene Officer will review and schedule an in-person meeting in the lab space to complete verification. Once completed, keep a copy of this form in the Lab Safety Manual.

		<i>EH&S Verification</i>
Principal Investigator		/
Department		/
Building/Room(s)		/
Planned Pyrophoric Materials		/
Description of storage space (glovebox, flammable cabinet, freezer, etc)		
Description of usage space (glove box, fume hood, etc)		
Description of Processes/Equipment planned for pyrophoric work		
Date of Last Inventory Certification (UC Chemicals>Inventory Summary)		
SOP completed and signed by PI?		

Approved Users

Name	Signed SOP?	Taken Flame Resistant Glove Training?	Received Flame Resistant Gloves from EH&S?	<i>EH&S Verification</i>

PI:
Chemical Hygiene Officer:

Date:
Date: