Pyrophoric Materials

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A. Purpose

Pyrophoric materials can ignite when exposed to air. Handling pyrophoric chemicals poses a significant hazard if proper precautions are not taken. The purpose of this policy is to ensure that Columbia University personnel use appropriate safety measures and fully understand emergency procedures when working with pyrophoric materials.

B. Applicability/Scope

This policy applies to all Columbia University personnel who handle, store or dispose of any pyrophoric chemicals.

C. Definitions and Background

Pyrophoric Material

Pyrophoric materials are chemicals that readily ignite when exposed to air. Many types of pyrophoric chemicals are present in Columbia University labs including:

- Organometallic compounds, including
  - Organomagnesiums (Grignard Reagents)
  - Organolithiums, such as t-butyllithium
  - Organozincs, such as diethylzinc
  - Aluminum alkyls, such as trimethyl aluminum
- Metallic hydrides, such as sodium hydride, potassium hydride, lithium aluminum hydride and some boranes
- Finely divided metals, such as: aluminum, lithium, magnesium, titanium, zinc, zirconium, sodium, and potassium

Two regulatory definitions for pyrophoric materials are listed below, from the Occupational Safety and Health Administration and the US Department of Transportation, respectively:

> "Pyrophoric" means a chemical that will ignite spontaneously in air at a temperature of 130°F (54.4°C) or below.

– 29 CFR 1910.1200(c)

> A pyrophoric material is a liquid or solid that, even in small quantities and without an external ignition source can ignite within 5 minutes after coming in contact with air when tested according to UN Manual of Tests and Criteria.

– 49 CFR 173.124 (b)(1)

Chemical Fume Hoods

Chemical fume hoods are engineering controls that are utilized as a means of preventing exposure to airborne workplace hazards. Chemical fume hoods protect workers against exposure to gases, chemical vapors and aerosols. Each lab's chemical fume hood must be certified annually and be in proper working order for chemical work to take place in the hood. Please review the Columbia University Chemical Fume Hood Policy for use and maintenance requirements at http://www.ehs.columbia.edu/fhPolicy.html. For questions about the status of your lab's chemical fume hood please contact a Research Safety Specialist.

Please note: In the event that your chemical fume hood had previously been used for radioactive isotopes, there must be no evidence of contamination, fixed or removable, before work with pyrophoric materials is performed in the chemical fume hood. If a chemical fume hood's radioactive history is unknown, please contact a Research Safety Specialist.

Glove Box
A glove box is an air tight enclosure with heavy rubber gloves used for manipulation of any items inside. As an engineering control, the glove box can provide protection for the user as well as an inert atmosphere for working with pyrophoric, air sensitive or water reactive materials.

Gas Cabinet
A gas cabinet is a fully enclosed, non-combustible and separately ventilated enclosure for storage of hazardous gasses. Any cylinder, larger than a lecture bottle, of pyrophoric gas must be stored in a gas cabinet with a sprinkler system.

Lecture Bottle
Lecture bottles are small compressed gas cylinders of about 13 inches in length and 1 inch in diameter.

D. Procedures

Precautions must be employed when using pyrophoric materials. The following sections describe the types of controls available to pyrophoric chemical users. Additionally, the next sections contain storage and disposal guidelines as well as emergency equipment and response information.

1. Chemical Substitution
Whenever possible, substitute an alternative material which is less dangerous in place of pyrophoric materials. Similarly, a safer solvent or mixture of a pyrophoric reagent can be chosen (e.g. using sodium hydride mineral oil dispersion instead of dry powder)

2. Engineering Controls

Engineering controls are used to remove or reduce the potential for exposure to a hazard or place a barrier between a worker and a hazard (NIOSH). Engineering controls for pyrophoric materials include glove boxes and chemical fume hoods (see Section C for definitions). A glove box with an inert atmosphere greatly reduces the hazard of spontaneous combustion by eliminating oxygen and moisture. Chemical fume hoods may be used as an alternative for pyrophoric liquids and solutions, but not for pyrophoric solids as the turbulence present may introduce enough additional oxygen at a sufficient rate to induce combustion.

3. Administrative Controls

Training

All laboratory workers are required to complete Laboratory Safety,Chemical Hygiene and Hazardous Waste Management Training prior to work in a laboratory. Training dates are available on the EH&S website http://www.ehs.columbia.edu/TrainingScheduleMC.html .

Additionally, specific training is required prior to work involving pyrophoric reagents. This training is available online at https://www.rascal.columbia.edu; course number TC1850 "Pyrophoric Materials Training." Live training is also available upon request by a group or department. Contact a Research Safety Specialist to set up a live session.

Technical training on specific procedures involving pyrophoric chemicals must be completed in the lab and documented (see section I). Typically, a PI or senior lab member trains new lab workers individually using a hands-on approach. Labs are advised to develop written training documents for all procedures involving pyrophoric materials. This affords the lab an ability to demonstrate that training was given, and protects the integrity of the procedure as it is passed along among workers. For reference, a pyrophoric safety bulletin describing basic manipulation of pyrophoric materials is posted on the EH&S website, as well as a safety video prepared by UCLA. http://www.ehs.columbia.edu/PyrophoricMaterials.html

Planning

When planning any procedure involving a pyrophoric chemical, researchers must review the Safety Data Sheet (SDS) and any technical guidance offered by the chemical's manufacturer. Conferring with experienced colleagues, as well as reviewing literature on similar procedures performed successfully elsewhere, can provide valuable guidance and should always be part of the experimental planning process when working with pyrophoric materials. It is crucial that the researcher attain a complete understanding of the risks and hazards associated with the use of all chemicals in their planned procedures.

In the planning stages of any procedure involving pyrophoric reagents, it is important to consider the following: the hazards present, the controls available to mitigate hazards, the equipment to be used, Personal Protective Equipment (PPE), emergency procedures, storage and disposal.

Practice
It is highly advantageous to perform "practice runs" for a given procedure. In a practice session, the pyrophoric chemical can be substituted with water or another non-hazardous substance. Repetitive practice develops confidence and calmness, and thus reduces the likelihood of a mistake during the actual procedure. Additionally, any flaws in the procedure can be identified and remedied through the use of practice runs.

Safe Work Practices
Safe work practices include institutional requirements and good habits which promote safety. The research and planning habits described above are considered safe work practices. The following are also safe work practices:

- Never work alone in a laboratory while handling hazardous materials
- Keep current with all training requirements
- Create and follow a written Standard Operating Procedure (SOP)
- Fully utilize all appropriate engineering controls
- Use the proper PPE, such as flame resistant lab coats
- Minimize hazards; see below
- Become familiar with fire and life safety equipment such as eye washes and fire extinguishing media
- Be prepared for emergencies

Notification
Never work alone in a laboratory while handling pyrophoric materials. Laboratory personnel must notify others working nearby prior to performing any work with pyrophoric chemicals. For each procedure, a worker must be accompanied by a trained colleague who is familiar with the hazards posed by pyrophoric reagents; and is versed in the appropriate emergency procedures.

Minimization of Hazards
Minimizing the hazard entails fully utilizing engineering and administrative controls and safe work practices. Removing all combustible materials from the work area, as well as selecting the most reliable tools, are both good ways to minimize the hazard. For example: selecting the best syringe minimizes the risk of air pocket formation or plunger slippage under inert gas pressure for transfer applications.

4. Personal Protective Equipment (PPE)

PPE begins with proper work attire. Long pants and closed-toed shoes are required for work in all Columbia University labs. The following additional personal protective equipment is required for any work involving pyrophoric materials:

- Non-synthetic clothing.
- Fire-resistant lab coat such as Nomex or Kevlar
- Nitrile gloves
- Splash goggles or safety glasses – ANSI standard rated
- Face shield when explosion or splash risk exists
- Keep long hair pulled back and remove any loose jewelry

It is important to note that nitrile gloves are combustible. Kevlar or leather gloves may be worn underneath the nitrile outer gloves. Although this may inhibit manual dexterity, it can provide some fire protection.

5. Emergency Equipment

Extinguishing Media
The primary risk when working with pyrophoric materials is fire. For an actively burning pyrophoric chemical, standard ABC fire extinguishers are not recommended as they can scatter the fire. Class D fire extinguishers and/or specialized extinguishing media are required for work involving pyrophoric reagents.

There are various types of class D extinguishing media available, including: sodium chloride, graphite and sand based blends. Many formulas consist of an inert powder and a polymer which melts to isolate the burning mass form oxygen. Using the proper delivery system and following the manufacturer's guidelines are necessary for the effective use of class D media. However, not all class D formulas are suitable for a given pyrophoric chemical. For example: some suppression agents can undergo an exothermic reaction with sodium hydride, leading to potential re-ignition or pressurization. It is prudent to carefully select a type of class D media based on the chemicals to be used.

Secondary fires, in which nearby combustible materials catch fire upon contact with burning pyrophoric materials, pose a significant risk when working with pyrophoric chemicals. Such cases result in combustible fires rather than a burning mass of pyrophoric material. Standard ABC extinguishers can be used on combustible fires.

Shower and Drench Devices
Overhead emergency showers and eye wash stations constitute standard emergency equipment for working with chemicals. Eye wash stations must be tested weekly by laboratory staff; overhead emergency showers are tested annually by Facilities.

6. Storage

The best place to store a pyrophoric chemical is in a glove box under an inert atmosphere. Pyrophoric reagents must be stored in their original containers. The original bottle can be stored

in a desiccator or in the manufacturer's original outer container (usually a large can). Outer containers must be clearly and accurately labeled. Chemical segregation rules must always be followed. Review sections 7 and 10 of the SDS for storage recommendations and incompatible materials.

Storage of pyrophoric materials in refrigerators is NOT recommended. Many pyrophoric chemicals are also water reactive; refrigerators do not provide a dry environment. Secondly, many pyrophoric reagents are stored as a solute in a flammable organic solvent; these solvents pose an explosion risk when stored in standard refrigerators. If refrigerated storage is necessary, pyrophoric materials must be stored in an explosion-proof refrigerator which has been specifically designated for pyrophoric chemicals.

Pyrophoric gas in a lecture bottle may be stored in a fume hood. Any larger cylinders containing pyrophoric gas must be stored in a ventilated gas cabinet equipped with a sprinkler system.

7. Emergency Response

Emergency preparedness is the most important part of an effective response. What to do in case of an emergency must be included in any SOP involving pyrophoric chemicals. Workers should be familiar with the location of emergency equipment such as fire extinguishers, eye wash stations and overhead emergency showers. The glove box or fume hood which is closest to these safety devices should be chosen for work involving pyrophoric reagents. During practice runs, conduct emergency drills and develop a plan of action.

Before starting a procedure, some steps can be taken to minimize hazards and enhance emergency response. First, any unnecessary flammable liquids or other chemicals should be removed from the work area. Combustible materials such as fabric, cardboard or paper should also be removed. Removing excess clutter in and around the work area is another way to minimize the danger of working with pyrophoric chemicals. Secondly, mobile safety equipment such as fire extinguishers, fire blankets and extinguishing media can be moved closer to the work area where they may be needed. Keeping a small beaker of sand or class D media in the fume hood can help to extinguish small needle tip fires.

8. Disposal

To minimize the hazards present in the lab, it is strongly recommended that ordering be limited to the minimum quantity of a pyrophoric reagent as needed at a given time. Disposal of expired, unused, partially used or empty bottles of pyrophoric chemicals must be considered in the planning stages of each procedure. It is prudent to rinse any syringes or lines with solvent, and to purge any partially full bottles with inert gas prior to disposal. Consult the Pyrophoric Materials Bulletin for more details on equipment cleanup and chemical disposal. Seal all waste containers and submit a Chemical/Hazardous Waste Pickup Form using the link below. Accurately fill out the form, including the chemical name, so that the personnel who service

your request are aware of the hazards. Proper storage must be maintained until the time of pickup, even for empty bottles.

http://vesta.cumc.columbia.edu/ehs/wastepickup/.

Responsibilities
It is the PI or Lab Manager's responsibility to ensure that a lab worker who plans on working with pyrophoric materials complies with the following:

- Current lab safety training
- Current pyrophoric materials training
- Documented task-specific training for handling pyrophoric reagents
- Development of written SOP for each procedure
- Full utilization and maintenance of engineering controls
- Full utilization of administrative controls
- Full utilization of PPE
- Selection of proper class D extinguishing media for the chemicals used
- Never work alone

E. Emergency Contacts

In the event of an emergency, please call the following numbers:

- **Morningside:** Call Public Safety (x99) & then call 911 for medical help. EH&S: 212-854-8749.
- **Medical Center:** Public Safety (305-7979) and then call NYPH EMS at 212-305-9999. EH&S: 212-305-6780.
- **NYSPI:** Contact Security at 212-543-5555*. EH&S: 212-305-6780.

In the event of a medical emergency, please seek medical attention at the following locations:

Campus	Hours	Faculty / Staff	Students
Medical Center	Business Hours	Workforce Health & Safety- Harkness Pavilion First Floor (212) 305-7580	Student Health Services - 60 Haven Avenue (212) 305-3400
	After Hours	NYPH Emergency Department - First Floor of the Vanderbilt Clinic (VC)	NYPH Emergency Department - First Floor of the Vanderbilt Clinic (VC)

Morningside	Business Hours	St. Luke's Hospital 1111 Amsterdam Avenue at 114th St, New York	Student Health Services - John Jay Hall, 3rd and 4th Floors (212) 854-2284
	After Hours		St. Luke's Hospital 1111 Amsterdam Avenue at 114th St, New York

F. Cross References – N/A

G. Medical Surveillance

In the event of personal exposure, seek medical attention immediately in accordance with Section F.

H. Recordkeeping

Laboratories are required to document any in-lab technical training for procedures involving pyrophoric chemicals. This is separate from the general laboratory safety, biosafety and pyrophoric materials training sessions (see section D). The form in section K can be used for this purpose.

I. Appendices

J. Forms Pyrophoric Tech Training Sheet.doc

K. References

Carnegie Mellon University Environmental Health & Safety: Pyrophoric Handling Policy, June 2010, Retrieved From: http://www.cmu.edu/ehs/chemical/pyrophorichandlingpolicy.pdf

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L. Acknowledgements

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APPENDIX A