ENVIRONMENTAL HEALTH AND SAFETY
University of Nebraska-Lincoln

Safe Operating Procedure

(Revised 8/24)

PYROPHORIC LIQUIDS AND SOLIDS AND SUBSTANCES THAT EMIT FLAMMABLE GASES WHEN IN CONTACT WITH WATER HAZARDS & RISK MINIMIZATION

Background

The United States Occupational Safety and Health Administration (OSHA) has adopted the following definitions as they pertain to this SOP.

- **Pyrophoric liquid or solid**. A liquid or solid which, even in small quantities, is liable to ignite within 5 minutes after coming into contact with air. OSHA also recognizes pyrophoric gases, which are addressed in the EHS SOP titled ***Hazards of Flammable Gases, Liquids & Aerosols.***
- **Chemicals which, in contact with water emit flammable gases**. Solid or liquid chemicals which, by interaction with water, are liable to become spontaneously flammable or give off flammable gases in dangerous quantities.

Categories, pictogram, signal words and hazard statements that will be found on the label and Safety Data Sheets (SDSs) are summarized in the table below.

Hazard Classification & Category	Pictogram	Signal Word	Hazard Statement
Pyrophoric			
Pyrophoric liquid, Category 1		Danger	Catches fire spontaneously if exposed to air
Pyrophoric solid, Category 1		Danger	Catches fire spontaneously if exposed to air
Substances that emit flammable gases when in contact with water			
Category 1		Danger	In contact with water releases flammable gases, which may ignite spontaneously

Category 2		Danger	In contact with water releases flammable gases
Category 3		Warning	In contact with water releases flammable gases

Hazards of Pyrophoric Chemicals

1. Liquids

While not exhaustive, pyrophoric liquids often include specific chemicals from the following chemical families:

- Alkyl metals (e.g., t-butyllithium, trimethylaluminum, and diethylzinc)
- Alkyl metal halides (e.g., diethylaluminum bromide)
- Alkyl magnesium halides 'Grignard reagents' (e.g., methylmagnesium bromide)
- Alkylphosphines (e.g., triethylphosphine)
- Boranes (e.g., borane dimethylsulfide complex)

The term 'organo' is sometimes used in place of 'alkyl'; for example 'organolithium.' The broad classification for alkylmetals is 'organometallics.'

In each of these categories, there are chemicals that are pyrophoric while others are not. Lower alkyl-substituted compounds are more likely to be pyrophoric while substitutions involving larger alkyl groups will tend to be more stable. Some pyrophoric liquids are dissolved in compatible flammable solvents to increase stability. Once the pyrophoric ignites, the solvent will also burn.

A unique hazard of pyrophoric liquid is that they are liquids. As such, they can be sprayed, splashed, and flow over surfaces. Elaborate procedures using syringes or cannula (double tipped needles) or displacement of liquids under a low-pressure stream of inert gas (e.g., nitrogen) are needed to transfer or manipulate the compound while excluding atmospheric air. Fire can result if there is a failure in a handling/manipulation procedure (e.g., a needle slipping from a container, a plunger being pulled from a syringe, over-pressurizing of a bottle, etc.).

2. Pyrophoric Solids

Pyrophoric solids include the following chemicals:

- White phosphorous
- Uranium IV oxide

- Super fine metal powders (e.g., iron, lead, nickel, platinum, aluminum)

White phosphorous ignites immediately and burns intensely on exposure to the atmosphere. Most metal powders can be pyrophoric if they are in the form of a fine powder. The risk increases if they do not have a protective oxide coating. The degree of reaction depends on the size of the particle, its distribution, and surface area. Some pyrophoric solids are packaged in inert atmospheres while others are dispersed in mineral oil or other diluent.

Hazards of Substances that Emit Flammable Gases When in Contact with Water

While not exhaustive, this category often includes specific chemicals from the following chemical families:

- Alkali metals (e.g., lithium, sodium, etc.)
- Metal hydrides (e.g., sodium hydride, lithium hydride, etc.)
- Complex metal hydrides (e.g., lithium aluminum hydride, sodium aluminum hydride, etc.)
- Calcium carbide

Many substances in this hazard category will react with moisture in the air; reactivity varies based on the chemical, its form, and the level of moisture in the air.

- Alkali metal hydrides are more reactive than other metals. Reactivity increases while moving down the periodic table. Lithium is the least reactive to moisture in the air and cesium is the most reactive. Francium is so reactive it is not commercially available. For all alkali metals, water will give a violent reaction producing flammable hydrogen gas that can then ignite. Depending on the circumstances, the ignition can be explosive.
- Most water reactive metals such as lithium and sodium can be purchased as ingots, cubes, and lumps and are packaged in inert atmospheres or immersed or dispersed in mineral oil or other protective liquid. Reactivity to moist air increases with smaller particle size/greater surface area exposed.
- Atmospheric moisture can vary widely. In the winter, relative humidity can be below 10% while in the spring or summer it can reach nearly 100%. A water-reactive chemical that is stable at one level of humidity may spontaneously ignite or ignite sooner in an environment where the humidity is higher. Where water-reactive chemicals are exposed to the atmosphere, be mindful of changes in atmospheric humidity.
- A couple of water-reactive materials bear special note. Calcium carbide will form small amounts of acetylene in contact with atmospheric moisture; but, in contact with water,

will emit significant amounts of this flammable gas. Potassium metal can form yellow, shock sensitive peroxides in storage. If this is detected, do not move or touch the chemical and notify the nearest supervisor.

Mitigating the Risks of Pyrophoric Liquids and Solids and Substances that Emit Flammable Gases When in Contact with Water

A written, comprehensive project-specific risk assessment with additional oversight is required for any experiment involving "Pyrophorics" and "Substances and mixtures which, in contact with water, emit flammable gases – Category 1." See the companion EHS SOP, ***Chemical Hazard Assessment and Risk Minimization***. A specific risk assessment with additional oversight may also be required for other categories of "Substances and mixtures which, in contact with water, emit flammable gases" depending on the specific hazards of an experiment or protocol, as described in the companion EHS SOP referenced above. General risk mitigation measures are as follows:

- Conduct a thorough literature search, including review of Safety Data Sheets, to establish a thorough understanding of the properties of the chemicals to be handled with particular consideration given to the procedures and tasks to be conducted. See also the following Laboratory Safety Colloquium archive presentations: ***Unstable, Reactive, and Energetic Compounds*** and ***Pyrophorics (Air-Sensitive) Chemical Safety***.

  Additional guidance is provided in the following Aldrich Technical Bulletins (available through the Sigma Aldrich web site): AL-134, *Handling Air Sensitive Reagents* and AL-164, *Handling Pyrophoric Reagents*. The University of California San Diego produced instructional videos that are available through the UCSD EHS web site: *Working with Pyrophoric Reagents* and *Working with Reactive Metals*. Another valuable publication is U.S. Department of Energy, *Handling Pyrophoric Reagents*, PNL18668, Contract DE-AC05-76RL01830, August 2009. Other resources include a video produced by Dartmouth, ***Handling Pyrophoric Materials***, available on YouTube (https://www.youtube.com/watch?v=iLMl10X0Naw) and another video produced by UCLA, ***Pyrophoric Liquid Safety***, also available on YouTube (https://www.youtube.com/watch?v=21iC4YEgOAs).

- Follow general safe chemical handling practices as described in the EHS SOP, ***General Guidance for Chemical Ordering, Receipt, Distribution, Use and Storage***.

- Observe all specific safety procedures established for the laboratory/procedure, as well as guidance provided by the chemical supplier. Practice your technique with a non-

hazardous material before handling and have your technique evaluated by an experienced person.

- Verify the accessibility and operability of a safety shower in the immediate work area.
- Remove all excess and nonessential chemicals and equipment/materials from the work area, particularly combustible and flammable materials.
- Purchase the most stable chemical that will do the job. Purchase those that contain stabilizing diluents or other hazard reducing additives.
- Keep amounts on-hand to a minimum.
- Conduct work on the smallest scale possible.
- Conduct operations in a manner to prevent exposure to the atmosphere. Several techniques, depending on the chemical identity, physical state, and quantity used are available. These techniques range from use of gas-tight syringes to glove boxes. If using a gas tight syringe technique, use a syringe with ample extra volume beyond the amount to be measured so that the syringe plunger is not withdrawn to near the end of the syringe barrel.
- When working in an inert environment, be aware that some pyrophoric chemicals will react with nitrogen.
- Quench contaminated glassware, wipes, spatulas, gloves, or septa under an inert atmosphere. When quenching residuals, use the least reactive chemical that will do the job.
- Use a fume hood for any work that cannot be done in a glovebox. Secure all apparatus including product containers where appropriate. Keep the sashes closed as much as possible.
- Use containers and dispensing equipment such as syringes, scoops or spatulas that the chemical supplier recommends.
- For all operations, make sure that the apparatus can adequately vent any gases generated.
- Do not use paper towels when cutting alkali metals unless the towel is quenched afterward. Alkali metal fragments can cause the towel to ignite after it has been disposed.
- Never reuse containers that once held pyrophoric chemicals or substances that emit flammable gases when in contact with water. Do not return excess chemical to the

original container. Small amounts of impurities introduced into the container may cause a fire or explosion.

- Store separate from all other chemicals. Store chemicals in an area that is not prone to water (e.g., away from sinks, under fume hoods that are plumbed with water, etc.).
- If packaged in a specially designed shipping/storage/dispensing container, ensure that the integrity of the container is maintained.
- If packaged under a protective liquid, ensure that sufficient protective liquid remains while the substance is stored. Do not store for prolonged periods.
- Do not wear synthetic clothing. Wear cotton or wool as these will not melt in a fire. Proper lab attire consists of closed-toed shoes and long pants supplemented with appropriate Personal Protective Equipment (PPE). See EHS SOP, ***Personal Protective Equipment for Chemical Exposures***.
    - Wear fire resistant lab coats. Note, these coats do not readily catch fire but pyrophoric liquids splashed on the coat will still burn.
    - Eye protection in the form of safety glasses with side shields coupled with a face shield is recommended.
    - Consider fire retardant gloves when handling these chemicals.
    - Other PPE may be appropriate depending on the specific operations and chemicals involved.