

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

(For assistance, please contact EHS at (402) 472-4925, or visit our web site at <http://ehs.unl.edu/>)

Background

Historically, pyrophoric chemicals were commonly defined as those that would ignite on exposure to air. The reaction could be to atmospheric oxygen, water vapor, or both. Water reactive chemicals were defined as those that reacted violently in contact with water. Under the newly adopted Globally Harmonized System (GHS) of classification and labeling of chemicals, these definitions have changed.

Under the GHS, a chemical is said to be “pyrophoric” if a small quantity of the material will ignite within 5 minutes after coming into contact with atmospheric oxygen. Ignition due to moisture in the air is no longer a part of the definition of pyrophoric.

The GHS classification “substances and mixtures which, in contact with water, emit flammable gases” includes those that will emit flammable gases due to moisture in the air. In some cases, the evolution of flammable gas is directly followed by fire which is why these materials were commonly considered ‘pyrophoric.’

If reaction with atmospheric moisture results in the evolution of a non-flammable gas (e.g., HCl), then the chemical is assigned to a different GHS classification (such as Toxic, Corrosive, etc.).

Because of the similarity in hazards and risk mitigation measures, this SOP addresses both GHS chemical classes of “pyrophorics” and “substances and mixtures which, in contact with water, emit flammable gases.” The GHS has one category for pyrophoric liquids and solids.

The GHS has three categories for “substances and mixtures which, in contact with water, emit flammable gases.”

- Category 1 – gases emitted ignite spontaneously or the rate of flammable gas evolution is ≥ 10 liters/kg of substance/minute
- Category 2 – rate of flammable gas evolution is ≥ 20 liters/kg of substance/hour
- Category 3 – rate of flammable gas evolution is ≥ 1 liter/kg of substance/hour

Both categories will be identified with the pictogram shown below. In addition, Section 2 of the Safety Data Sheet (SDS) will include one of the hazard statements indicated below.



Pyrophoric

- H250 Catches fire spontaneously if exposed to air

Substances and mixtures which, in contact with water, emit flammable gases

- H260 In contact with water releases flammable gases which may ignite spontaneously
- H261 In contact with water releases flammable gas

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.

3. Flammable Gases that Ignite in the Presence of Air

The GHS does not have a class for pyrophoric gases although National Fire Protection Association (NFPA) Standards still use the term "pyrophoric gases." Instead, gases that ignite on exposure to air will be listed as "Flammable." Silane will ignite when exposed to air under most environmental conditions. Diborane, arsine, phosphine may ignite on exposure to air depending on humidity and temperature. Diborane will ignite spontaneously in moist air. All pyrophoric gases are toxic by inhalation. Some, like phosphine, are highly toxic. Special

considerations for use and storage of this category of gases is discussed in more detail in the EHS SOP, ***Gases Under Pressure Hazards & Risk Minimization***.

Extinguishing Agents for Pyrophorics

For gases, close the valve at the cylinder if it is safe to do so. If not, evacuate the area. Most burning pyrophoric gases are difficult to extinguish. Silane is reported to be impossible to extinguish.

Most pyrophoric solids react violently with water. Most pyrophoric liquids are also either water reactive or dissolved in solvents that do not mix with water. Water will only spread the fire. Thus, do not use wet chemical, water, or foam as an extinguishing agent. Use sand or powdered limestone to smother the fire.

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

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 Pyrophorics 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 – GHS 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*. Special considerations for pyrophoric gases are discussed in the EHS SOP, ***Gases Under Pressure Hazards & Risk Minimization***. Another valuable publication is U.S. Department of Energy, *Handling Pyrophoric Reagents*, PNL18668, Contract DE-AC05-76RL01830, August 2009.
- Follow general safe chemical handling practices as described in the EHS SOP, ***General Guidance for Chemical Ordering, Receipt, Distribution, Use and Storage***.
- Ensure that an appropriate fire extinguisher is readily available. For more guidance see the EHS SOP, ***Fire Safety – General Prevention and Extinguishing*** and the EHS web-based training program titled ***Fire Extinguisher Training***.
- 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 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 chemicals in glove boxes or desiccators when possible. Where storage in a glove box or desiccator is not possible, displace any residual air with an inert gas, seal the lid and wrap with parafilm. Store in metal cabinets separated 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. Some reactive metals are packaged, shipped, and stored under oil or kerosene. Ensure that sufficient protective liquid remains in the container while the material is stored.
- 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***.
 - Wear fire resistant lab coats. Note, these coats do not readily catch fire but pyrophoric liquids splashed on the coat will still burn.
 - At a minimum, eye protection in the form of safety glasses with side shields is necessary. If there is a splash hazard, upgrade to goggles and a face shield.
 - Consider fire retardant gloves when handling these chemicals.
 - Other PPE may be appropriate depending on the specific operations and chemicals involved.