

Pyrophorics

1. Purpose / Background

The purpose of this document is to provide information and procedures to assure that pyrophorics are used safely and to outline practices to be followed to prevent injury and damage associated with pyrophoric explosions per the MIT Environmental, Health and Safety (EHS) Policy and in accordance with the Guiding Principles in Support of the EHS Policy. To view the EHS Policy and Guiding Principles, go to http://ehs.mit.edu/ > About >> Policies (Keyword Search: Policies)

Pyrophoric substances are liquids, solids, or gases that will ignite spontaneously in air at or below 130 °F (54.4 °C). To receive the pyrophoric classification under GHS a chemical must ignite within 5 minutes in air. However, chemicals that ignite after 5 minutes also pose a significant risk to users and should be handled as pyrophoric. Many pyrophorics are also water reactive. Many reducing agents are pyrophoric and water reactive due to their rapid oxidation by oxygen or moisture in the air. Serious burns could occur to personnel handling a pyrophoric if it were to spontaneously combust.

Water-reactive substances are substances that react with water to release a gas that is either flammable or a health hazard. When water contacts a water-reactive substance, enough heat may be generated to cause spontaneous combustion or an explosion. Examples of water-reactive chemicals include alkali metals (sodium, potassium, and lithium), anhydrides, certain carbides, hydrides, sodium hydrosulfite, and similar chemicals.

2. Scope

This SOP is a generic guideline that can be used to aid MIT laboratories and shops that use pyrophorics to develop a material-specific and experiment-specific SOP for their work.

This SOP does not cover the use of pyrophoric gases. The use of pyrophoric gases is covered in the Compressed Gases SOP.

3. Prerequisites

Laboratories working with pyrophorics must have a Chemical Hygiene Plan. Shops working with pyrophorics are under the MIT Hazard Communication Program. Anyone working with a pyrophoric liquid or solid must have a specific written handling, transfer and storage plan.

4. **Procedures**

4.1 General Use Procedures

Appendix A lists some pyrophoric substances. Some common pyrophorics include alkyl lithiums, trialkylaluminum reagents, and alkylboranes. Appendix C lists common Pyrophoric and Water-Reactive Chemicals at MIT. The most pyrophoric of the lithium reagents is t-butyllithium, although concentrated n-butyllithium (approximately 10 M) is also pyrophoric.

Most incidents occur when pyrophorics are transferred to an appropriate reaction flask, for hydrolysis and /neutralization with adequate cooling. Incidents in laboratories occur because this procedure has been done improperly. Root causes range from choosing the wrong solvent, to improper cooling, or even lack of an adequate quantity of solvent to provide enough of a heat sink (even though it has been cooled). Most incidents resulting from pyrophoric compounds have been a result of incorrect procedure during the quenching process versus actual experimentation with the material. Prior to performing this practice, consult with the principal investigator and/or laboratory director for guidance.

- Information: Acquire a safety data sheet (SDS) and manufacturer technical bulletins for all pyrophorics being used. Due to the severe potential hazards of pyrophorics, carefully review the handling and storage procedures and become familiar with the chemical and physical properties of each substance before beginning work. Always review the incompatibility with other substances and the conditions to which the compounds are sensitive. Always read the manufacturers' recommendations contained in supplementary documents, such as technical bulletins. Contact the EHS Office to review new uses of pyrophorics.
- **Purchase:** In obtaining pyrophorics, a careful analysis should be made of how much is needed for the time period of the research, factoring in allowable storage quantities noted in Appendix D. Experiments should be designed to keep the lowest possible amount on hand.
- **Training**: Anyone using pyrophorics must have thorough and adequate training and knowledge of the hazards and practices and procedures for working with them safely. If you are unsure of any of the procedures get assistance. All users of pyrophorics must be fully qualified and experienced laboratory workers or working under direct supervision of experienced workers. See section 6 for detailed training requirements.
- **Storage quantities**: According to the Massachusetts State Building Code 780 CMR Table 307.1(1), pyrophoric substances are permitted only in buildings equipped throughout with an automatic sprinkler system in accordance with 780 CMR 906.2.1, and the quantities of pyrophorics are limited to four pounds per control area (see Appendix D).
- **SOP**: A laboratory specific SOP is required for use of pyrophorics.
- **Personal Protective Equipment**: Flame resistant (FR) lab coats are required when handling pyrophoric substances, including chemicals that release

flammable gases that may ignite spontaneously and self-heating chemicals that may catch fire outside of a glove box. FR lab coats should also be worn when working with chemicals that react violently with water or release flammable gas, or when performing potentially vigorous reactions.

- Protective eyewear is required when handling pyrophoric and waterreactive materials. Fully enclosed safety goggles or a face shield are preferred, as they offer greater facial protection than safety glasses.
- Gloves are required when handling pyrophoric and water-reactive materials. It is recommended that Nomex gloves be worn between two pairs of nitrile gloves for fire protection purposes.
- Clothing made from polyester and other synthetic fabrics and loose clothing should not be worn. Always wear long pants and closed toe shoes within the lab. Loose or long hair should be tied back to prevent ignition in the event of a flash fire.

• Engineering Controls:

- Pyrophorics should be used in a chemical fume hood (over a spill tray) using techniques that prevent the material from contacting air or in an inert-atmosphere glove box according to the manufacturers recommendations. Aldrich Technical Bulletins AL-164 and AL-134 provide detailed instruction on using standard syringe and double-tipped-needle transfer techniques which prevents contact with air. Some pyrophorics must be handled in a gas-tight syringe to prevent exposure to air.
- Aldrich sells a portable controlled-atmosphere chamber known as an AtmosBag that can be sealed, purged, and inflated with an inert gas.
- If use of the pyrophoric substance in a chemical fume hood is appropriate according to the manufacturer's recommendations, then the sash should be as far down as feasible. If there is a potential explosion hazard, then isolate the process behind a blast shield, portable safety shield, or a barricade secured to an immovable object. Again, techniques must be used to prevent contact with air.
- It is recommended that tongs, stopcock turners, or mechanical arms be used for manipulating experiments at a safer distance.

• Work Practice Controls

- Laboratories working with pyrophoric materials should develop material specific SOPs to assure their safe handling.
- Always follow the manufacturer's recommendations for use and storage. Aldrich Technical Bulletin AL-164 Handling Pyrophoric Reagents and AL-134 Handling Air-sensitive Reagents provide detailed instructions for handling pyrophorics.
- Only experienced laboratory workers should handle pyrophorics.
- Use and purchase pyrophorics in the smallest quantities necessary and design experiments on as small a scale as possible.

- A small beaker of sand can be used to extinguish any fire that occurs at the syringe tip and to receive any last drops of reagent from the syringe.
- Never return excess pyrophorics to the original container since small amounts of impurities introduced into the container may cause a fire or explosion.
- Remove all excess chemicals and equipment from the work area to reduce the risk of involving other chemicals in case of a fire or explosion.
- Do not mix with other chemicals without prior knowledge of the hazards involved, and taking appropriate precautions. Minimize quantities as much as possible for such reactions. Prior to introducing pyrophoric materials with other compounds, researchers should document the expected chemical reaction in a laboratory notebook.
- \circ Vacuum pumps should be rated for use with pyrophorics.
- Do not allow pyrophorics to contact combustible material, such as paper or cardboard.
- Transport and store the glass pyrophoric bottle in the original metal shipping container.
- All of the pyrophoric substance should be used for a chemical reaction. Any residual or trace material must be transferred to an appropriate reaction flask for hydrolysis and/neutralization with adequate cooling. Never open a container with residual or trace amounts of pyrophorics to the atmosphere.
- Ensure that heating methods used do not cause or increase the potential for ignition.
- Never leave potentially hazardous experiments unattended.

4.2 General Storage and Disposal Procedures

Storing pyrophorics should be part of a comprehensive chemical storage plan that is outlined in the Chemical Storage SOP. The SDS for each material should be read to determine specific storage recommendations or special storage conditions.

- Some pyrophoric materials must be stored under an atmosphere of inert gas, under kerosene, or under another solvent, as indicated in the manufacturer's instructions and MSDS.
- Once opened, containers should be dated. Ensure that enough solvent remains to cover the material in the container during storage.
- Pyrophics reagents from Aldrich are packaged in Sure/Seal bottles which can be handled and stored with exposure to atmospheric moisture or oxygen. The reagent can be dispensed using a syringe or double-tipped needle inserted through the hole in the metal cap. Check the crown cap and liner conditions regularly to make sure that they are in good conditions to provide tight seals.
- Pyrophorics should be stored and transported in the original metal shipping container.

- The storage area should be conspicuously marked to indicate that pyrophorics are being stored.
- Pyrophorics are permitted only in buildings equipped throughout with an automatic sprinkler system and the quantities are limited to four pounds per control area (See Appendix D: Massachusetts State Building Code 780 CMR Table 307.1(1)

Disposal: Excess pyrophoric chemicals should be treated as hazardous waste. Due to their properties, special procedures may be required for waste collection, and labs may incur disposal fees based on factors outlined below.

- Disposal of empty pyrophoric containers: Under an inert atmosphere, add dry inert solvent (preferably the same solvent used for the original reagent) to empty the pyrophoric container and rinse three times. Neutralize or hydrolyze the rinsate. Red tag the empty bottle as hazardous waste.
- If there is a need to remove large quantities of pyrophoric material, contact EHS to arrange for disposal, as a fee may be applied depending on the volume. The more toxic and hazardous the chemical and the larger the bottle, the higher the cost tends to be. NEVER put these in the "less than 90 day" storage areas where flammable solvents may be present. Nonreturnable pyrophoric gas cylinders will also incur a cost at the time of disposal. Contact EHS for disposal rates and information on the removal process.
- Certain metal powders, such as fine aluminum powder, should be submerged in oil prior to waste collection from the lab. Debris with aluminum powder may be collected with a thin coating of oil and kept separate from other debris waste streams.
- Reactive metals, such as lithium, potassium and magnesium, should also be submerged under oil and handled as hazardous waste. Contact EHS for additional guidance.

4.3 General Emergency Procedures

Plan ahead for possible emergencies involving pyrophorics. All personnel who work in areas where pyrophorics or explosives are used should be trained in how to respond to potential emergencies.

- Prior to using pyrophorics, consult the SDS for the appropriate clean-up supplies and ensure that they are readily available. Spill control materials are designed to be inert and unreactive with the reagent.
- Before using pyrophorics, ensure that dry sand, powdered lime, Met-L-X or Lith-X suppression material or a Class D fire extinguisher is nearby (within arm's length) as fire-extinguishing medium. For pyrophoric spills, do not use water or carbon dioxide-based extinguishers since they can enhance the combustion of the compounds.
- DO NOT USE a CO₂ extinguisher to attempt to quench a fire with pyrophoric reagents, this can greatly enhance the problem.

- Notify people in the area that a spill has occurred. For a large spill, turn off sources of ignition and vacate the lab immediately. Dial 100 for emergency assistance (Off campus, dial 617-253-1212).
- In case of fire or explosion, activate the fire alarm and dial 100 or 617-253-1212 from a safe location.
- In case of skin contact, wash the affected area thoroughly with water for at least 15 minutes and seek immediate medical attention by calling 100 from a MIT phone or 617-253-1212 from a cell phone. Always know the location of the nearest eyewash and shower and how to use the emergency equipment. Keep the area clear at all times. It is best to use the chemical fume hood closest to the safety shower to perform the work.

5. Roles & Responsibilities

5.1 The EHS Office is responsible for:

- Providing General Chemical Hygiene Training (web-based or classroom) and MIT Overview HAZCOM training that includes information on chemical hazards.
- Maintaining up to date guidance pertaining to pyrophorics.
- Reviewing SOPs and new uses of pyrophorics.
- Addressing questions or concerns pertaining to pyrophorics.
- Assisting with inspections of use and storage areas for pyrophorics.

5.2 PI/Supervisors are responsible for:

- Ensuring SOPs for pyrophoric materials specific to the laboratory are developed.
- Ensuring those individuals that they supervise who work with pyrophorics receive adequate training (see Section 6.0 for training requirements.)
- Ensuring that pyrophorics are used and stored safely in the laboratory/work areas that they supervise.
- Ensuring pyrophorics are used and stored in the smallest quantities necessary in the work areas that they supervise.
- Ensuring appropriate PPE is available for work with pyrophorics.

5.3 The DLC EHS Coordinator or Chemical Hygiene Officer is responsible for:

- Addressing questions or concerns regarding the use or storage of pyrophorics, and consulting with the EHS Office if necessary.
- Inspecting chemical storage areas, including the storage areas of pyrophorics, twice a year during Level II inspections; notifying the laboratory personnel and the PI/Supervisor of problems found so that they can be corrected or prevented; and updating the PI Space Registration if pyrophorics are routinely used or stored in the lab.

5.4 The EHS Representatives are responsible for:

• Assisting the PI/Supervisors with the safe use and storage of pyrophorics in the work area. Specific duties may include periodically inspecting use and storage areas and keeping an inventory of pyrophorics.

5.5 Individuals using pyrophorics are responsible for:

- Knowing and following the pyrophorics SOPs established in their laboratory/work area.
- Assuring that they have adequate training.
- Using materials in accordance with training guidance provided, such as SOPs.
- Reporting any incidents, problems or concerns with handling materials to PI.
- Wearing the PPE that is specified.

6. Training

All laboratory personnel working with pyrophorics must have completed General Chemical Hygiene Training (web-based or classroom) and Lab-Specific Chemical Hygiene Training.

The Lab-Specific Chemical Hygiene Training, performed by a laboratory's PI or EHS representative, should include the following information if pyrophorics are used in the laboratory/work area:

- The hazards and safe use of pyrophorics.
- The location and function of specialized equipment needed for the safe use and storage of pyrophorics.
- Procedures to be used in case of an emergency with pyrophorics.
- The location of SDSs and SOPs for pyrophorics.
- Knowledge of appropriate PPE.

For non-laboratory personnel that use chemicals in their work area, the required training is called "General HAZCOM Training", and it is offered through the EHS Office.

Awareness level training should be given to others who work in areas where pyrophorics are present. Laboratories or DLCs desiring additional training for special or unusual applications of pyrophorics may contact the EHS Office for help in developing and implementing training specific to their needs.

7. Monitoring Requirements

Work areas where pyrophorics are used and stored should be inspected at least twice a year during the Level II inspections to assure that they are being used and stored safely and in accordance with the rules established for the area.

8. Record Management

The DLC EHS Coordinator and the EHS Office shall maintain records of Level II inspections of storage areas containing pyrophorics. All records related to the use and storage of pyrophorics should be maintained per the Records Retention SOP.

9. References

The following references are available through the EHS Office:

9.1 Standards

- OSHA 1910.1450 Occupational Exposure to Hazardous Chemicals in Laboratories
- OSHA 1910.106 Flammable and Combustible Liquids
- Massachusetts State Building Code 780 CMR Table 307.1(1)

9.2 Other SOP/SOGs

To view the SOPs/SOGs go to <u>https://ehs.mit.edu/sops/</u> and search for the SOP/SOG listed. MIT Certificates are required to view SOPs/SOGs.

- EHS-0001: Compressed Gases
- EHS-0053: Chemical Storage
- EHS-0053: Flammable and Combustible Liquids
- EHS Administrative SOP 04-0044: Records Retention

9.3 Supplementary Documents

- MIT Environment, Health and Safety Policy
- MIT HAZCOM Program
- Aldrich Technical Bulletin AL-134, Handling Air-Sensitive Reagents
- Aldrich technical Bulletin AL-164, Handling Pyrophoric Reagents
- "Prudent Practices for the Disposal of Chemicals from Laboratories" published by the National Academy Press
- Appendix B: Pyrophoric and Water-Reactive Chemical Safety Guide

9.4 Helpful Websites

OSHA Regulations and Technical Manuals: <u>http://www.osha.gov</u>

10. Definitions

10.1 Safety Data Sheet (SDS)

A written document that outlines health and safety information for a hazardous chemical. A SDS is prepared in accordance with requirements of OSHA 29 CFR 1910.1200 Hazard Communication.

10.2 Mixture

Any combination of two or more chemicals provided that the combination is not, in whole, or part, the result of a chemical reaction.

10.3 Pyrophoric Substances

Liquids or solids that will ignite spontaneously in air at or below 130°F (54.4 °C).

10.4 Unstable (reactive)

A chemical which in the pure state, or as produced or transported will vigorously polymerize, decompose, condense, or will become self-reactive under conditions of shock, pressure, or temperature.

10.5 Use

Packaging, handling, reacting, emitting, generating as a byproduct, or transferring.

10.6 Water-reactive substances

Substances that react with water to release a gas that is either flammable or a health hazard. When water contacts a water-reactive substance enough heat may be generated to cause spontaneous combustion or an explosion.

Appendix A: Examples of Pyrophoric Substances

1. Alkyls and aryls (metal and nonmetal):

- a. Butyllithium, CH₃(CH₂)₃Li
- b. diethylzinc,(C₂H₅)₂Zn
- c. ethyllithium, CH₃CH₂Li
- d. ethyl sodium,CH₃CH₂Na (and other sodium alkyls)
- e. tributyl aluminum, (CH₃CH₂CH₂CH₂)₃Al
- f. triethyl aluminum, (C₂H₅)₃Al
- g. triethylarsine,(C₂H₅)₃As
- h. triethylborane,(C₂H₅)₃B
- i. triethyl phosphine $(C_2H_5)_3P$

2. Carbonyls (metal):

- a. cobalt carbonyl, Co₂(CO)₈
- b. nickel carbonyl, Ni(CO)4
- c. iron carbonyl, Fe(CO)5

3. Gases:

- a. diborane (borane), B₂H₆
- b. dichloroborane, BCl2H
- c. dichlorosilane, SiH₂Cl
- d. disilane,Si₂H₆
- e. silane, SiH4
- f. phosphine, PH₃
- 4. Grignard Reagents (organomagnesium halides, RMgX):
 - a. Methylmagnesium bromide, CH₃MgBr

5. Hydrides (metal and nonmetal):

- a. arsine hydride, AsH₃
- b. aluminum borohydride, Al(BH₄)₃
- c. boron hydrides, BH₃, B₂H₆, B₂₀H₂₆ and other boranes (borane-phosphorous trifluoride BH₃-PF₃
- d. lithium aluminum hydride, LiAlH₄
- e. lithium hydride, LiH
- f. phosphine hydride, PH₃
- g. sodium borohydride, NaBH₄
- h. sodium hydride, NaH

6. Metal powders:

a.	aluminum, Al	g.	platinum, Pt
b.	cobalt, Co	h.	sodium, Na
C.	iron, Fe	i.	titanium, Ti, including titanium (II) chloride TiCl ₂
d.	lead, Pb	j.	tin, Sn
e.	magnesium, Mg	k.	zinc, Zn
f.	manganese, Mn	Ι.	zirconium, Zr

7. Phosphorous (white), P₄ {synonym: phosphorous (yellow)}

Appendix B: Pyrophoric and Water-Reactive Chemical Safety Guide

Classification

Pyrophoric substances are liquids, solids, or gases that will ignite spontaneously in air at or below 130 °F (54.4 °C). To receive the pyrophoric classification under GHS a chemical must ignite within 5 minutes in air. However, chemicals that ignite after 5 minutes also pose a significant risk to users and should be handled as pyrophoric.

Water-reactive substances are substances that react with water or moisture to release a gas that is either flammable or a health hazard. When water contacts a water-reactive substance, enough heat may be generated to cause spontaneous combustion or an explosion. The guidelines here refer to water-reactive substances that have a risk of igniting on contact with moisture, not those that only release toxic gases.

Engineering Controls

General guidance for handling pyrophoric and water-reactive chemicals is outlined below. However, many factors must be considered when determining what additional controls are required, including but not limited to the specific pyrophoric chemical(s) being used, type of application, and other hazards. For example, semiconductor research can involve pyrophoric materials that are also highly toxic, requiring additional controls. Contact your EHS coordinator or the EHS Office for more specific guidance on appropriate controls based on your lab's research.

Depending on the materials and process, pyrophoric and water-reactive materials should be used in a chemical fume hood (over a spill tray) using techniques that prevent the material from contacting air or in an inert-atmosphere glove box according to the manufacturer's recommendations.

Before using pyrophoric reagents refer to the Aldrich Technical Bulletins AL-164 and AL-134, which provide detailed instructions on using standard syringe and double-tipped needle transfer techniques to prevent contact with air. Some pyrophoric and water-reactive materials must be handled in a gas-tight syringe to prevent exposure to air.

Personal Protective Equipment (PPE)

Flame resistant (FR) lab coats are required when handling pyrophoric substances, including chemicals that release flammable gases that may ignite spontaneously and self-heating chemicals that may catch fire outside of a glove box. FR lab coats should also be worn when working with chemicals that react violently with water or release flammable gas, or when performing potentially vigorous reactions.

DOC #:	EHS-0043

Protective eyewear is required when handling pyrophoric and water-reactive materials. Fully enclosed safety goggles or a face shield are preferred, as they offer greater facial protection than safety glasses.

Gloves are required when handling pyrophoric and water-reactive materials. It is recommended that Nomex gloves be worn between two pairs of nitrile gloves for fire protection purposes.

Clothing made from polyester and other synthetic fabrics and loose clothing should not be worn. Always wear long pants and closed toe shoes within the lab. Loose or long hair should be tied back to prevent ignition in the event of a flash fire.

Fire Extinguishing

If your lab plans to, or currently uses pyrophoric compounds, it is recommended that you ensure the appropriate extinguishing agent is available; for example, a Class D extinguisher, sand or a Met-L-X or Lith-X suppression material.

Waste Management Guidelines

Excess pyrophoric chemicals should be treated as hazardous waste. Due to their properties special procedures may be required for waste collection and labs may incur disposal fees based on factors outlined below.

Contact EHS if several bottles are removed from storage at one time, as a fee may be applied depending on the volume. The more toxic and hazardous the chemical and the larger the bottle, the higher the cost tends to be.

Nonreturnable pyrophoric gas cylinders will also incur a cost at the time of disposal. Contact EHS for disposal rates and information on the removal process.

Certain metal powders, such as fine aluminum powder, should be submerged in oil prior to waste collection from the lab. Debris with aluminum powder may be collected with a thin coating of oil and kept separate from other debris waste streams.

Reactive metals, such as lithium, potassium and magnesium, should also be submerged under oil and handled as hazardous waste. Contact EHS for additional guidance.

Additional EHS resources:

- Reactive Waste: <u>https://ehs.mit.edu/ignitable-reactive-toxic-corrosive/</u>
- Non-returnable Cylinder Disposal: <u>https://ehs.mit.edu/chemical-safety-</u>program/compressed-gas-cylinder-safety/

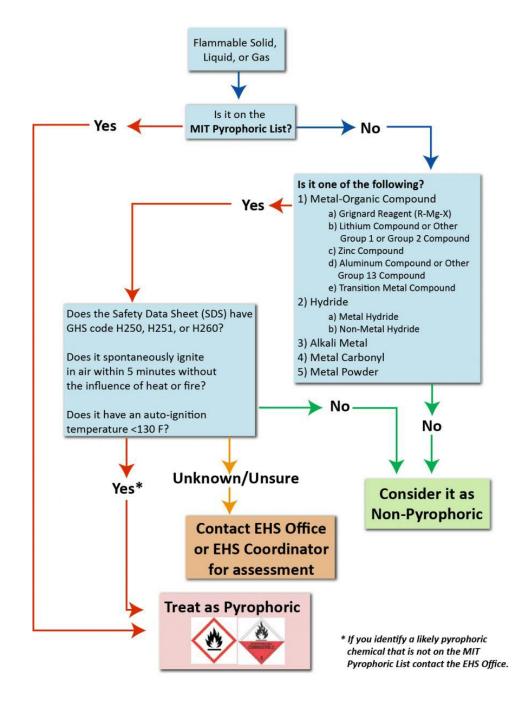
DOC #:	EHS-0043	Title:	Pyrophorics	Page #	13 of 18

Lab Specific Standard Operating Procedures (SOPs)

A laboratory specific SOP is required for use of pyrophoric materials. Contact your DLC's EHS Coordinator or the EHS Office for assistance.

Identifying Pyrophoric and Water-Reactive Materials

Each researcher is responsible for determining if the chemicals used are pyrophoric or waterreactive. To determine if a flammable solid, liquid, or gas is pyrophoric or could ignite on contact with moisture, do the following:



An official hardcopy of this document exists in the EHS Office or on the EHS website. External links are subject to change, please contact <u>environment@mit.edu</u> if you encounter a broken link. See Legal Disclaimer at: <u>http://ehs.mit.edu/legal-disclaimer</u>

Appendix C: Common Pyrophoric and Water-Reactive Chemicals at MIT

Classification: Pyrophoric substances are liquids, solids, or gases that will ignite spontaneously in air at or below 130 0F (54.4 0C). Water-reactive substances are substances that react with water or moisture to release a gas that is either flammable or a health hazard. When water contacts a water-reactive substance, enough heat may be generated to cause spontaneous combustion or an explosion. Flame resistant (FR) lab coats are required when handling pyrophoric substances, including chemicals that release flammable gases that may ignite spontaneously and self-heating chemicals that may catch fire (*highlighted blue below*). FR lab coats should also be worn when working with chemicals that react violently with water or release flammable gas (*highlighted yellow*), or when performing potentially vigorous reactions.

Key Phrases: SDSs do not always accurately classify chemicals as pyrophoric. Look both for pyrophoric classifications as well as other key phrases indicative of spontaneously combustible or violent reactions. Examples include "extremely flammable", "catches fire spontaneously", and "reacts violently with air or water". These phrases should trigger a closer look at other safety data sources or outreach to the EHS Office for assistance.

GHS Hazard Statements: The following hazard statements, found in section 2 of the SDS, indicate that the chemical exhibits pyrophoric or water-reactive characteristics that may warrant FR lab coat use.

H220: Extremely flammable gas. FR lab coat	H251: Self-heating: may catch fire. FR lab coat required.
required.	
H250: Catches fire spontaneously if exposed	H261: In contact with water releases flammable gases.
to air. FR lab coat required	
H260: In contact with water releases	HNOC: Reacts violently with water
flammable gases which may ignite	
spontaneously. FR lab coat required.	

	Category/Ty	pe	Example Chemicals	CASNO	H250	H251	H260	H261	HNOC	H220
		-	ALUMINUM BOROHYDRIDE	16962-07-5			Х			
			CALCIUM HYDRIDE	7789-78-8			Х			
			DIISOBUTYLALUMINUM HYDRIDE	1191-15-7	х		Х	х		
			LITHIUM ALUMINUM HYDRIDE	16853-85-3			Х			
			LITHIUM BOROHYDRIDE	16949-15-8			Х			
			LITHIUM HYDRIDE	7580-67-8			Х			
	Met	al Hydrides	POTASSIUM HYDRIDE	7693-26-7			Х			
			SODIUM BOROHYDRIDE	16940-66-2			Х			
			SODIUM HYDRIDE	7646-69-7			Х			
			SUPER-HYDRIDE (LITHIUM TRIETHYLBOROHYDRIDE)	22560-16-3			Х			
			SODIUM TRIACETOXYBOROHYDRIDE	56553-60-7				х		
			SODIUM TRIETHYLBOROHYDRIDE	17979-81-6				Х		
		Arsenic Compounds	ARSINE	7784-42-1						х
			9-BORABICYCLO [3.3.1]NONANE	280-64-8	х		Х			
			BORANE TETRAHYDROFURAN COMPLEX	14044-65-6			Х			
			BORANE TRIFLUORIDE	7637-07-2			Х			
			DIBORANE	19287-45-7	х					Х
		Boron Compounds	DICHLOROBORANE	13701-67-2	х					
Hydridae		Boron compounds	POLYBORANES		х					
Hydrides			TRIBUTYLBORANE	122-56-5	х					
			TRIETHYLBORANE	97-94-9	Х					
		TETRABUTYLAMMONIUM BOROHYDRIDE	33725-74-5				Х			
			TETRAFLUOROBORIC ACID-DIETHYL ETHER COMPLEX	67969-82-8				х	х	
			TETRAMETHYLAMMONIUM TRIACETOXYBOROHYDRIDE	109704-53-2				х		
	Non-Metal		DI-T-BUTYLMETHYLPHOSPHINE	6002-40-0	Х					
	Hydrides		DI-TERT-BUTYLPHOSPHINE	819-19-2	х					
	,		DICHLOROISOPROPYLPHOSPHINE, 97%	25235-15-8			Х		х	
		Phosphorus	DIPHENYLPHOSPHINE	829-85-6	Х					
		-	PHOSPHINE	7803-51-2						Х
		Compounds	TRI-N-BUTYLPHOSPHINE	998-40-3	Х					
		-	TRI-TERT-BUTYLPHOSPHINE	13716-12-6	х					
			TRIETHYL PHOSPHONE	554-70-1	х					
			TRIBUTYLPHOSPHINE	998-40-3	х					
			DICHLOROSILANE	4109-96-0				Х		Х
		Silicon Compounds	DISILANE	1590-87-0						Х
		Sincon compounds	METHYL SILANE	992-94-9					х	Х
			SILANE	7803-62-5	х					
			TRICHLOROSILANE	10025-78-2	х				х	

An official hardcopy of this document exists in the EHS Office or on the EHS website. External links are subject to change, please contact <u>environment@mit.edu</u> if you encounter a broken link. See Legal Disclaimer at: <u>http://ehs.mit.edu/legal-disclaimer</u>

	DOC #:	EHS-0043	Title: Pyrophorics	Page #	15 of 18	
--	--------	----------	--------------------	--------	----------	--

Category/Type	Example Chemicals	CASNO	H250	H251	H260	H261	HNOC	H220
	ALUMINUM	7429-90-5	х			х	х	
Metal Powders (Excluding Oxides)	BARIUM	7440-39-3			х	х		
NOTE: Many motal pourdors procent special storage and	CADMIUM	7440-43-9	x					
NOTE: Many metal powders present special storage and	CALCIUM	7440-70-2	х			х		
handling concerns when finely divided, including	CERIUM	7440-45-1	х					
hazards such as air- or water-reactivity or explosive dust	CESIUM	7440-46-2			х			
generation. Whether a given metal powder exhibits	CHROMIUM	7440-47-3	х					
	COBALT	7440-48-4	х					
these properties depends on multiple factors, including	EUROPIUM	7440-53-1	Х		х			
but not limited to particle size, surface area, moisture	HAFNIUM	7440-58-6	х					
level, purity, etc.	IRIDIUM	7439-88-5	х		-			
	IRON H251	7439-89-6		х				
	LEAD	7439-92-1	х					
Please contact your EHS Coordinator or the EHS Office	MAGNESIUM	7439-95-4	х		х		х	
for assistance when working with small-particle-size	MANGANESE	7439-96-5			х			
metal powders.	NICKEL	7440-02-0	х					
metur powders.	PALLADIUM	7440-05-3	х					
	PLATINUM	7440-06-4	X					
	PLUTONIUM	7440-07-5	X					
	RHODIUM	7440-16-6	х					
	RUBIDIUM	7440-17-7			X			
	STRONTIUM	7440-24-6	- <u>.</u>		х			
	TANTALUM	7440-25-7	X					
	TECHNETIUM THORIUM	7440-26-8	X					
		7440-29-1	X					
	TITANIUM URANIUM	7440-32-6 7440-61-1	X		Х			
	VANADIUM	7440-61-1	X X					
	ZINC	7440-62-2			х		х	
			X				*	
	ZIRCONIUM	7440-67-7	Х		х			

Category/Type	Example Chemicals	CASNO	H250	H251	H260	H261	HNOC	H220
Non-Metals	WHITE PHOSPHORUS (PHOSPHORUS TETRAMER)	12185-10-3	х					

Metal Halide	TITANIUM (II) CHLORIDE	10049-06-6	х			

Alkali Metals (Group 1)	LITHIUM	7439-93-2		Х	Х	
	POTASSIUM	7440-09-7		Х	Х	
	SODIUM	7440-23-5		х	х	

	COBALT CARBONYL	10210-68-1		Х		
Metal Carbonyls	CYCLOPENTADIENYL IRON DICARBONYL DIMER	12154-95-9		х		
	DISODIUM TETRACARBONYL FERRATE DIOXANE COMPLEX	59733-73-2	х			
	IRON CARBONYL	13463-40-6	х			
	NICKEL CARBONYL	13463-39-3	х			

	Category/Type	Example Chemicals	CASNO	H250	H251	H260	H261	HNOC	H220
		ALLYLMAGNESIUM BROMIDE	1730-25-2	Х		х		Х	
		ALLYLMAGNESIUM CHLORIDE	2622-05-1	х	1	х		Х	
		BUTYLMAGNESIUM CHLORIDE	693-04-9	х		х		х	
		CYCLOHEPTYLMAGNESIUM BROMIDE	78378-12-8			х			
		ETHYLMAGNESIUM BROMIDE	925-90-6			х		х	
		ISOBUTYLMAGNESIUM BROMIDE	926-62-5			х			
	Grignard Reagents (R-Mg-X)	ISOBUTYLMAGNESIUM CHLORIDE	5674-02-2			х			
		ISOPROPYLMAGNESIUM CHLORIDE	1068-55-9			х	Х		
		METHYLMAGNESIUM BROMIDE	75-16-1			х		Х	
Metal- Organic		METHYLMAGNESIUM IODIDE	917-64-6		1	х		Х	
		SEC-BUTYLMAGNESIUM CHLORIDE	15366-08-2	х		х	х	х	
		VINYLMAGNESIUM BROMIDE	1826-67-1			х		х	
Compounds		2,2-DIMETHYLPROPYLMAGNESIUM CHLORIDE	13132-23-5				х	Х	
Compounds		2,2,6,6-TETRAMETHYLPIPERIDINYLMAGNESIUM CHLORIDE LITHIUM CHLORIDE COMPLEX	898838-07-8					х	
		PROPYLMAGNESIUM CHLORIDE	2234-82-4				х		
		SEC-BUTYLMAGNESIUM CHLORIDE LITHIUM CHLORIDE COMPLEX	1032768-06-1				Х	Х	
		(TRIMETHYLSILYLMETHYL)MAGNESIUM CHLORIDE	13170-43-9					Х	
		BIS(CYCLOPENTADIENYL)MAGNESIUM	1284-72-6	х			Х	Х	
		ETHYLLITHIUM	811-49-9	х			Х		
		HEXYLLITHIUM	21369-64-2	х		х			
		LITHIUM DIISOPROPYLAMIDE	4111-54-0	х	I I			х	
		LITHIUM DIMETHYLAMIDE	3585-33-9	х			Х		

An official hardcopy of this document exists in the EHS Office or on the EHS website. External links are subject to change, please contact <u>environment@mit.edu</u> if you encounter a broken link. See Legal Disclaimer at: <u>http://ehs.mit.edu/legal-disclaimer</u>

	DOC #:	EHS-0043	Title: Pyrophorics	Page #	16 of 18	
--	--------	----------	--------------------	--------	----------	--

	Category/Type	Example Chemicals	CASNO	H250	H251	H260	H261	HNOC	H220
		LITHIUM TERT-BUTOXIDE	1907-33-1	х				х	
		METHYLLITHIUM	917-54-4	Х		Х			
		N-BUTYLLITHIUM	109-72-8	х			х	Х	
		PHENYLLITHIUM	591-51-5	х			х		
Metal-		POTASSIUM ETHOXIDE	917-58-8	Х				Х	
	Lithium Compounds &	POTASSIUM METHOXIDE	865-33-8	Х				Х	
Organic	Other Group 1 and 2 Compounds	POTASSIUM TERT-BUTOXIDE	865-47-4			Х			
Compounds	Other Group 1 and 2 Compounds	PROPYLLITHIUM	1888-75-1	Х		х			
Compounds		SEC-BUTYLLITHIUM	598-30-1	х		х			
		SODIUM CYCLOPENTADIENIDE	4984-82-1			х			
		SODIUM METHOXIDE	124-41-4	х				х	
		SODIUM TERT-BUTOXIDE	865-48-5	Х				Х	
		TERT-BUTYLLITHIUM	594-19-4	Х		х			
		LITHIUM 2,2,6,6-TETRAMETHYLPIPERIDIDE	38227-87-1				Х		
		LITHIUM AMIDE	7782-89-0				Х	Х	
		SODIUM AMIDE	7782-92-5				х		
		DIETHYL ZINC	557-20-0	Х		Х			
	Zine Commounde	DIMETHYL ZINC	544-97-8	Х		х			
	Zinc Compounds	1-ADAMANTYLZINC BROMIDE	312624-15-0					Х	
		CYCLOPROPYLZINC BROMIDE	126403-68-7					х	
		ALUMINUMTRIETHANIDE	97-93-8	Х		Х		Х	
		DIISOBUTYLALUMINUM CHLORIDE	1779-25-5	Х		х		Х	
	Aluminum Compounds &	TRIBUTYLALUMINUM	1116-70-7	Х		Х			
	Other Group 13 Compounds	TRIMETHYLALUMINUM	75-24-1	х		х		х	
	other Group 15 compounds	TRIMETHYLGALLIUM	1445-79-0	х		х		х	
		TRIMETHYLINDIUM	3385-78-2	х		х	х		
	Transition Metal Compounds	BIS(2-METHYLALLYL) (1,5-CYCLOOCTADIENE)RUTHENIUM(II)	12289-94-0				х		

Page #

17 of 18

Appendix D: Storage Quantities

780 CMR: Massachusetts State Board of Building Regulations and Standards (The Massachusetts State Building Code)

Table 307.1(1) (Reproduced in part) Exempt Amounts of Hazardous Materials, Liquids and Chemicals Presenting a Physical Hazard Maximum Quantities Per Control Area^{a,k}

Title:

Material	Class	Use	Storage ^b			Closed Systems ^b			Open Systems ^b		
		Groups	Solid pounds (cubic feet)	Liquid gallons (pounds)	Gas (cubic feet)	Solid pounds (cubic feet)	Liquid gallons (pounds)	Gas cubic feet	Solid pounds (cubic feet)	Liquid gallons (pounds)	
Pyrophoric		H-2	4 ^{e,h}	(4) ^{e,h}	50 ^{e,h}	1 ^h	(1) ^h	10 ^{e,h}	0	0	
Water Reactive	3	H-3	5 ^{d,e}	(5) ^{d,e}	NA	5 ^d	(5) ^d	NA	1 ^d	(1) ^d	
	2	H-3	50 ^{d,e}	(50) ^{d,e}		50 ^d	(50) ^d		10 ^d	(10) ^d	

Note a. For use of control areas, see 780 CMR 414.2.

Note b. The aggregate quantity in utilization and storage shall not exceed the quantity listed for storage.

Note c. The quantities of alcoholic beverages in retail sales occupancies shall not be limited provided the liquids are packaged in individual containers not exceeding 1 gallon. In retail sales and storage occupancies, the quantities of medicines, foodstuffs and cosmetics, containing not more than 50%, by volume of water-miscible liquids and with the remainder of the solutions not being flammable, shall not be limited provided that such materials are packaged in individual containers not exceeding one gallon.

Note d. Maximum quantities shall be increased 100% in buildings equipped throughout with an automatic sprinkler system in accordance with 780 CMR 903.3.1. Where note e. also applies, the increase for both notes shall be applied accumulatively.

Note e. Quantities shall be increased 100% when stored in approved cabinets, gas cabinets, fume hoods, exhausted enclosures, or safety cans as specified in the fire prevention code listed in Appendix C. Where noted, also applies, the increase for both notes shall be applied accumulatively.

Note f. The permitted quantities shall not be limited in a building equipped throughout with an automatic sprinkler system in accordance with 780 CMR 903.3.1.

DOC #:	EHS-0043	Title:	Pyrophorics	Page #	18 of 18

Note g. A dust explosion potential is considered to exist where 1 pound or more of combustible dust per 1,000 cubic feet of volume is normally in suspension or could be put into suspension in all or a portion of an enclosure of inside pieces of equipment. This also includes combustible dust which accumulated on horizontal surface inside buildings or equipment and which could be put into suspension be an accident, sudden force or sudden explosion.

Note h. Permitted only in buildings equipped throughout with an automatic sprinkler system in accordance with 780 CMR 903.3.1.

Note i. One pound of black sporting powder and 20 pounds of smokeless powder are permitted in sprinklered or unsprinklered buildings. **Note j.** Containing not more than the exempt amounts of Class I-A, Class, or Class flammable liquids.

Note k. Quantities in parenthesis indicate quantity units in parenthesis at the head of each column. 1 cubic feet = 0.028 m^3 ; 1 pound = 0.45 kg; 1 gallon = $.00379 \text{ m}^3$