**Standard Operating Procedure**

**Quenching and Disposal of Liquid Pyrophoric Materials**

**Examples: tert-ButylLithium, sec-ButylLithium, n-Butyllithium, DiethylZinc, Organoaluminum compounds (as Et3Al, Et2AlCl, EtAlCl2, Me3Al), Raney Nickel catalyst.**

Water-Reactive Materials, such as lithium, sodium, cesium, lithium aluminum hydride, potassium hydride, are designated by the following H codes: H260 and H 261. Please refer to the hazardous operation SOP “Quenching of Water Reactive Materials” for the chemicals.

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***This is an SOP template and is not complete until:*** *1) lab-specific information is entered into the box below 2) lab specific protocol/procedure is added to the protocol/procedure section and   
3) SOP has been signed and dated by the PI and relevant lab personnel.*

Print a copy and keep with your   
*Chemical Hygiene Plan* and/or *Lab Safety Resources Binder*

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| --- | --- |
| **Department:** | Click here to enter text. |
| **Date SOP was approved by PI/lab supervisor:** | Click here to enter a date. |
| **Principal Investigator:** | Click here to enter text. |
| **Lab Safety Coordinator/Lab Manager:** | Click here to enter text. |
| **Lab Phone:** | Click here to enter text. |
| **Office Phone:** | Click here to enter text. |
| **Emergency Contact:** | Click here to enter text. |
| *(Name and Phone Number)* |
| **Location(s) covered by this SOP:** | Click here to enter text. |
| *(Building/Room Number)* |

**Type of SOP:** Process Hazardous Chemical Equipment

1. **Purpose**

This SOP covers the precautions and safe handling procedures for the Quenching of Liquid Pyrophoric Materials.

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If you have questions concerning the applicability of any recommendation or requirement listed in this procedure, contact the Principal Investigator/Laboratory Supervisor of your laboratory or EH&S.

1. **Physical & Chemical Properties/Definition of Chemical Group**

For physical and chemical properties on pyrophoric materials, please refer to specific Safety Data Sheets (SDS) of chemicals in use (See Section 11 – SDS Location).

1. **Potential Hazards**

When exposed to moisture or air, these reagents may ignite spontaneously. When quenching pyrophoric materials, the individual hazards of the pyrophorics and the solvent, as well as the hazard of the mixture, should all be considered, and procedures for safe quenching should reflect this consideration.

As defined by the Globally Harmonized System of Classification and Labeling of Chemicals (GHS), pyrophorics and self-heating substances are designated by one or more of the following H codes:

Pyrophorics

H250 Catches fire spontaneously if expose to air

Self-Heating Substances

H251 Self-heating; may catch fire

H252 Self-heating in large quantities; may catch fire

Please, review the SDS of any chemical before use (see Section 11 – SDS Location)

1. **Safety Data Sheet (SDS) Location**

Online SDS can be accessed at (<http://oregonstate.edu/ehs/sds>). A hard copy can be found at Oak Creek Building with Environmental Health & Safety.

1. **Engineering Controls**

The following is the set of engineering controls required when quenching pyrophoric materials:

* Work under an inert atmosphere (e.g., argon, nitrogen) using a Schlenk line, in a glove box, vacuum manifold, or any enclosed inert environment.
* Use a clean fume hood, preferably with the sliding sash windows or a glove box.
* If procedure is done in the fume hood, use the sash as a safety shield. For hoods with a horizontal sliding sash, position the sash all the way down, stand behind the sliding windows and reach around to perform the manipulations required. For hoods with vertical sliding sash, keep the sash as low as possible.
* Face shields are to be used when there is no protection from the hood sash or when the hood sash is open.
* Keep the materials under inert atmosphere when not in use.
* Remove any flammables (squirt bottles containing solvents, oil baths) and combustibles (Kimwipes, paper towels) from the area that will be used for the quenching.

1. **Personal Protective Equipment (PPE)**

At a minimum, the following PPE must be worn at all times:

**Eye Protection**

1. ANSI Z87.1-compliant safety glasses with side shields, or chemical splash goggles.

* Ordinary prescription glasses will NOT provide adequate protection unless they also meet ANSI standard and have compliant side shields.

1. If the potential for explosion/splashing exists, and adequate coverage is not provided by the hood sash, a face shield should be worn.

**Skin Protection**

1. Flame-resistant lab coat (Nomex IIIA, NFPA 2112) should be worn when working with pyrophoric and self-healing materials.
2. Gloves are required when handling hazardous materials. Refer to the specific chemical SDS for information on glove selection.
3. Long pants, closed-toe/closed-heel shoes, covered legs, and ankles. Cotton-based, non-synthetic clothing should be worn.
4. **Administrative Controls:**

* Anyone who uses Pyrophoirics is required to review this SOP and the attached Safety Data Sheet (SDS) prior to work.
* Keep quantities to a minimum and only order what you will be using.
* An eyewash must be available in the room with a safety shower accessible nearby.

1. **Best Practices for Safe Handling:**

Pyrophoric reagents can be handled and stored safely as long as all exposure to atmospheric oxygen and moisture or other incompatible chemicals is avoided. Never leave a container with a residue of a pyrophoric material open to the atmosphere.

Lab-specific information on handling and storage may be included in Section 12 - Protocol/Procedure section.

**Handling Pyrophoric Liquids**

• There are two basic techniques to transfer pyrophoric liquids: the syringe and the cannula needle (over-pressure transfer). The syringe must only be used for small quantities (less than 20 mL). To conveniently transfer 20 mL or more of reagent at once, the cannula technique must be used.

• A glovebox or a Schlenk line in a fume hood with inert gas flow will be necessary. The sure-seal cap system provides a convenient method for storing and dispensing air-sensitive reagents.

• Pyrophoric solids must be transferred under an inert atmosphere in a glove box.

• Pyrophoric gases must be handled in compliance with the California Fire Code, Chapter 41.

• Eliminate or substitute for a less hazardous material when possible.

• Design your experiment to use the least amount of material possible to achieve the desired result.

• Do not exceed the scale of procedures specified in Protocol/Procedure section without the approval of the PI.

• Verify your experimental set-up and procedure prior to use.

• Know the location of the nearest eyewash, safety shower, and fire extinguisher before beginning work.

• Upon leaving the work area, remove any personal protective equipment worn and wash hands.

• At the end of each project, thoroughly decontaminate the work area according to the material being handled.

**Storage of Pyrophoric Materials**

• Keep the material under inert atmosphere when not in use.

• Store minimal amounts of pyrophoric chemicals. Containers carrying pyrophoric materials must be clearly labeled with the correct chemical name and hazard warning in English.

• Inert gas-filled desiccators or glove boxes are suitable storage locations for most materials.

• If pyrophoric materials are received in specially designed shipping, storage or dispensing container (such as the sure-seal cap system), ensure that the integrity of that container is maintained.

• Take extreme care to prevent containers of pyrophorics from leaking or breaking. Secondary containment is required for storing and transporting pyrophoric materials. Use corrosion and shatter-resistant containers.

• Pyrophoric chemicals that require refrigeration must be stored in a flammable rated refrigerator. Materials should be in a clearly labeled secondary container on the top shelf of the refrigerator. Do not store materials in the fridge door.

• Ampules must be stored and transported in secondary containers (even in glove boxes). Take extreme care while handling ampules outside of the glove box, keep in mind that these glass containers are very fragile.

• Ensure that a sufficient protective solvent, oil, kerosene, or inert gas remains in the container while the material is stored.

1. **First Aid Procedures**

If an accident happens the following documents must be completed:

* Online OSU HR Advocate Public Incident Reporting Form within 24 hours of the incident
* If the employee’s incident resulted in the need for medical treatment, have the employee complete the worker section of the SAIF 801 Form and fax to risk management at 541-737-4855 within 24 hours.

**In case of skin contact**

If skin contact occurs, and/or skin or clothing are on fire, immediately drench in the safety shower with copious amounts of water for no less than 15 minutes to remove any remaining contaminants. If possible to do so without further injury, remove any remaining jewelry or clothing.

**In case of eye contact**

Rinse thoroughly with plenty of water using an eyewash station for at least 15 minutes, occasionally lifting the upper and lower eyelids. Remove contact lenses if possible.

<http://ehs.oregonstate.edu/sites/ehs.oregonstate.edu/files/pdf/si/eyewash_and_safety_shower_si.pdf>

**If swallowed**

Do NOT induce vomiting unless directed otherwise by the SDS. Never give anything by mouth to an unconscious person. Rinse mouth with water.

**Needle stick/puncture exposure**

Wash the affected area with antiseptic soap and warm water for 15 minutes. For mucous membrane exposure such as eyes, mouth and/or nose, flush the affected area for 15 minutes using an eyewash station.

**If inhaled**

Move into the freshair.

1. **Chemical Spill**

**OSU Chemical Spill Safety Instruction**: <http://ehs.oregonstate.edu/sites/ehs.oregonstate.edu/files/pdf/si/spill_response-chemicals_si.019.pdf>

**Pyrophoric Spill Response**

* Disposal of Pyrophoric Reagents
* Never leave a container with a residue of a pyrophoric material open to the atmosphere.
* Any unused or unwanted pyrophoric materials must be destroyed by following the specific destruction procedure(s) included in your “Hazardous Operation SOP – Quenching of Pyrophoric Materials”. As an alternative to quenching, remember that pyrophoric chemicals can be disposed of as hazardous waste (contact EH&S for guidance on disposal).
* Waste materials generated must be treated as a hazardous waste.
* The empty container must be rinsed three times with a COMPATIBLE solvent; leave it open in the back of the hood overnight. The rinse solvent must be transferred in and out of the container under an inert atmosphere using the syringe or cannula technique. Solvent rinses and water rinse must be disposed of as hazardous waste.
* As an alternative, unrinsed empty containers can be disposed of through EH&S as hazardous waste. The unrinsed empty containers must be capped.
* Do not mix with incompatible waste streams.
* Decontamination of containers in order to use them for other purposes is not permitted.
* Report the spill to 541-714-SAFE.

**Pyrophoric Fire Response**

* Call 911 for emergency assistance and for assistance with all fires, even if extinguished.
* If the spill ignites, and if you are trained and you feel comfortable to do so, consider extinguishing the fire with an appropriate fire extinguisher. Only dry chemical fire extinguishers should be used (classes ABC or D). Do not use a CO2 extinguisher.
* A can of Met-L-X or dry sand in the work area, within arm’s reach, might be helpful to extinguish any small fire as it can smother the flames.
* Do not use water to extinguish a pyrophoric chemical fire as it may enhance the intensity of the fire. An exception to this would be in the case of skin contact or ignited clothing/skin. In these cases rinsing any unreacted chemical off is of primary importance.
* Be AWARE: Small flames at the tip of the needles can be produced – always expect this to occur, and do not panic. The can of Met-L-X/sand is in the hood to quickly extinguish those small flames.

1. **Decontamination/Waste Disposal Procedure**

Lab-specific information on decontamination may be included in the Protocol/Procedure section.

* Wearing proper PPE, laboratory work surfaces should be cleaned at the end of each workday.
* Store liquid wastes in designated waste containers. Dispose of according the OSU EH&S hazardous waste guidelines.

**Disposal of Pyrophoric Reagents**

* Never leave a container with a residue of a pyrophoric material open to the atmosphere.
* Any unused or unwanted pyrophoric materials must be destroyed by following the specific destruction procedure(s) included in your “Hazardous Operation SOP – Quenching of Pyrophoric Materials”.
* Waste materials generated must be treated as a hazardous waste.
* The empty container must be rinsed three times with a COMPATIBLE solvent; leave it open in the back of the hood overnight. The rinse solvent must be transferred in and out of the container under an inert atmosphere using the syringe or cannula technique. Solvent rinses and water rinse must be disposed of as hazardous waste.
* Do not mix with incompatible waste streams.
* Decontamination of containers in order to use them for other purposes is not permitted.

**Label Waste**

* Affix an EH&S hazardous waste label on all waste containers (<http://ehs.oregonstate.edu/sites/ehs.oregonstate.edu/files/pdf/hwlabelfull.pdf>) as soon as the first drop of waste is added to the container.

**Store Waste**

* Store hazardous waste in closed containers, in secondary containment and in a designated location. (<http://ehs.oregonstate.edu/sites/ehs.oregonstate.edu/files/pdf/si/waste_hazardous_disposal_si.pdf)>.
* Waste must be under the control of the person generating & disposing of it

**Dispose of Waste**

* Dispose of regularly generated chemical waste within 90 days
* Put in a waste request at: <http://ehs.oregonstate.edu/waste>

1. **References**

[Include any references useful to employees]

[Sigma-Aldrich Technical Bulletin AL-134](https://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/Aldrich/Bulletin/al_techbull_al134.pdf) – Handling Air-Sensitive Reagents

[Sigma-Aldrich Technical Bulletin AL-164](https://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/Aldrich/Bulletin/al_techbull_al164.pdf) – Handling Pyrophoric Reagents

University of Minnesota, Environmental Health and Safety – “[Pyrophoric Chemicals Guide](https://www.google.com/url?client=internal-uds-cse&cx=000747455861485679472:bqyjqaw6sp8&q=http://www.me.umn.edu/intranet/safety/doc/Pyrophoric%2520Chemicals%2520Guide.docx&sa=U&ved=2ahUKEwjQirSIl6HkAhXoFjQIHbAhCnAQFjAAegQIAxAB&usg=AOvVaw0pnB6xupRki_lEz4dnLxKZ)”

UCLA, Environmental Health and Safety – [“Pyrophoric Liquid Safety Video”](https://www.youtube.com/watch?v=21iC4YEgOAs)

University of Mass Amherst – [SOP Pyrophoric Liquids and Solids](https://ehs.umass.edu/sites/default/files/Pyrophoric%20Liquids%20or%20Solids%20SOP.pdf)

[UCSD - Transferring Pyrophoric Chemicals Video](https://www.youtube.com/watch?v=WUHrzcEunNY&feature=youtu.be)

[UCSD - Working with Pyrophoric Reagents Video Part 1](https://www.youtube.com/watch?v=3_cBVfYVAC8&feature=youtu.be)

1. **Protocol/Procedure for: Quenching of Water Reactive Materials**

**Preparation**

*[List any other particular preparation requirements needs for this procedure (e.g., location of spill kit or keep water or ignition sources away from procedure area]*

* Know the location of the nearest fire extinguisher, eyewash, and safety shower before beginning work.
* Have a small can of Met-L-X or dry sand in the work area, within arm’s reach.
* Solvents must be dry.
* Glassware must be dry before using. Either “flame” dry or dry in an oven at a minimum temperature of 100° C for at least two hours.
* Remove all other flammable/combustibles materials from the hood to reduce the hazard in case of a fire. Make adjacent lab workers aware that you will be working with pyrophoric chemicals.

**Quenching of pyrophoric liquids, such as, but not limited to,sec-BuLi, n-BuLi, Grignard reagents, remaining in bottle or left after reactions**

Up to 500 mL of pyrophoric materials in carrier solvent. Quenching of pyrophoric materials in amounts greater than 500 mL at a time is not permitted.

Conduct in a clean fume hood with the sash closed using the Schlenk techniques, or an inert atmosphere glove box.

If using outside an inert atmosphere glove box, ensure the receiving vessel is dry and a blanket of inert gas is kept over the air-sensitive chemicals.

Note on Glassware Size: If quenching 100mL of pyrophoric solution, the pyrophoric material will be diluted in 500mL of inert solvent to start the quenching procedure (20% wt solution). In this case, the required size for the quenching vessel is 1L, no less. If quenching 500 mL of pyrophoric material, the required size for the quenching vessel is 2L, no less.

**Quenching in a FUME HOOD using a Schlenk line**.

General considerations: Quenching procedures usually involve the reaction of the pyrophoric material, under inert atmosphere and on an ice bath, with a reagent that has a reactive hydroxyl group.

Any reaction or suspension containing these reagents MUST be quenched carefully! All transfers must be done under inert atmosphere using the syringe or cannula techniques.

Addition of material must be done SLOWLY, under adequate stirring/mixing.

Whenever quenching, be sure that it is not done in a sealed vessel as pressure will build up. The best situation is to have an inert gas flowing in with a small exit needle connected to a bubbler.

If you’re quenching in a RB flask or any floating vessel in a bath, clamp it. If the solution level is low, you can dilute it with some inert solvent such as toluene or hexane first to less than 20% wt.

Procedure: Transfer the diluted solution to the quenching vessel, place ice under the flask, and turn on the stirrer.

Before proceeding with the quenching of the pyrophoric solution, proceed with the cleaning of the empty bottle.

The empty container should be rinsed three times with an inert dry COMPATIBLE solvent such as toluene or hexane. The rinse solvent must be transferred in and out of the container under an inert atmosphere.

After the empty container is triple-rinsed, remove the SureSeal cap and it should be left open in the back of a hood overnight.

Dispose of the solvent rinse as hazardous waste.

Proceed with the quenching of the pyrophoric solution by adding isopropanol slowly to the quenching vessel using a syringe or an addition funnel, under adequate stirring, until no more bubbling is observed.

Keep the solution cool (50°C or below) during the quenching process by controlling the feed rate of the alcohol.

Once you've added the isopropanol, add the following solvents in sequence, using the same step-wise caution: ethanol, methanol, and water.

Be Very Careful with the addition of water! Even after methanol has been added, the lithiate can still react violently with water, especially is there hasn't been sufficient mechanical stirring of the solution. Add water in small aliquots. The addition of water does not need to be conducted under an inert atmosphere. The use of a syringe (plastic or glass) is recommended.

Once the addition of water is complete, let the solution temperature come back to room temperature while stirring.

Stir for an additional 2 hours before disposing of the aqueous organic waste.

- If quenching in a FUME HOOD using dry ice -

Place dry ice in a container and add a stir bar. Pyrophoric liquids in this section can be quenched by slowly adding the dilute solution directly onto dry ice, then adding a mildly reactive quenching agent such as methanol. Once the addition of the dilute solution is complete, let the solution temperature come back to room temperature under stirring.

Stir for an additional 2 hours before disposing of the aqueous organic waste.

- If quenching in a GLOVE BOX -

General considerations:

Any reaction or suspension containing these reagents MUST be quenched carefully! Addition of solvents should be done SLOWLY with adequate stirring/mixing.

If the glove box is equipped with a fridge, DO NOT open the fridge during the quenching process.

Procedure:

1. Turn OFF the glove box circulation.
2. Remove bottle or reaction vessel cap and add a stirrer if necessary.
3. Typically, a solution of less than 20%wt of pyrophoric in an inert solvent (such as dry and degassed hexane or heptane) is created, followed by the slow addition of dry and degassed isopropanol, under adequate stirring until no more bubbling is observed.
4. Place a cap on the quenching vessel and put the bottle/vessel in a zip-top bag before taking it out of the glove box.
5. Move the quenching vessel to a clean fume hood. Always place the quenching vessel in a secondary container for transfer to the fume hood.
6. Purge the glove box for 20-30 minutes.
7. Continue the quenching procedure in a clean fume hood with sash closed.
8. Under adequate stirring, add water SLOWLY to the quenching solution until no more bubbling is observed. This step does not need to be conducted under an inert atmosphere. The use of a syringe (plastic or glass) is recommended.
9. Be Very Careful with the addition of WATER! Even after isopropanol has been added, the lithiate can still react violently with water, especially is there hasn't been sufficient mechanical stirring of the solution. Therefore the water should be added in small aliquots.
10. Once the addition of water is complete, stir for an additional 2 hours before disposing of the aqueous organic waste.
11. The empty container should be rinsed three times with an inert dry COMPATIBLE solvent such as toluene or hexane.
12. After the empty container is triple-rinsed, it should be left open in the back of a hood overnight.
13. Solvent rinses should be disposed of as hazardous waste.
14. **Training Requirements**

Before working with quenching, the lab worker must have the approval of the designated person who shall provide specific training according to this SOP and in understanding the MSDS provided by the manufacturer. The lab worker must complete EH&S Laboratory Safety, Hazardous Waste, and Safety data sheets training prior to working with any chemicals. The lab worker should provide documentation that they understand the hazards and has been trained in how to work with pyrophoric safely.

**Documentation of Training**

* Prior to conducting any work with pyrophorics, designated personnel must provide training to their laboratory personnel specific to the hazards involved in working with this substance, work area decontamination, and emergency procedures.
* The Principal Investigator must provide this SOP and a copy of the SDS (can be available online) available to all laboratory personnel.
* The Principal Investigator must ensure that his/her laboratory personnel have attended appropriate laboratory safety training or refresher training.

**Principal Investigator SOP Approval**

By signing and dating here the designee certifies that the Standard Operating Procedure (SOP) for *Quenching and Disposal of Liquid Pyrophoric Materials* is accurate and effectively provides standard operating procedures for laboratory personnel.

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Signature Printed Name/Title Date

I have read and understood the content of this SOP:

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| **Name** | **Signature** | **Date** |
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