**Standard Operating Procedure (SOP) –** *Quenching of Pyrophoric Substances*

***Section 1 – Process***

Two methods are presented for the quenching and disposal of pyrophoric materials. The first method is recommended to quench unspent pyrophoric material. The second method should ONLY be used for small amount of material and concerns decontaminating glassware that has been used to handle pyrophoric materials.

Relevant reagents include:

* ***Organolithium reagents*** - typically in hydrocarbon solvents. Note: *tert*-butyllithium solutions are highly pyrophoric.
* ***Organomagnesium reagents*** - including Grignard reagents (RMgX) - Typically in hydrocarbon solvents. Neat reagents are pyrophoric.
* ***Organoaluminum reagents*** - Neat or in hydrocarbon solvents. Neat reagents are highly pyrophoric.
* ***Organozinc reagents*** - Neat reagents are pyrophoric.
* ***Boranes*** - Neat reagents are pyrophoric.
* ***Metal Hydrides*** – *e.g*. CaH2, NaH
* ***Group 1 metals*** – Li, Na, K

*Method 1: Particularly for large scale quenches*

The pyrophoric material to be quenched is initially transferred to a Schlenk flask, or round-bottom flask equipped with a vacuum adapter. Solids, such as Na metal, may be suspended in toluene or another high-boiling, non-reactive solvent to facilitate stirring during the quenching process. Pyrophoric solutions should be diluted to approximately 1 M with dry toluene, neat pyrophoric reagents must be diluted.

The flask is then placed under an inert atmosphere of N2 (use Ar for Li metal) using a bubbler to vent those gasses evolved during the quenching process. The inert atmosphere prevents solvents from catching fire if the quenching mixture should become hot. The flask is cooled to 0 °C followed by slow addition of isopropanol. Isopropanol is used as an initial quenching agent because it reacts less vigorously than water does with reducing materials.

ONLY after the addition of isopropanol to the quenching mixture no longer results in a vigorous reaction, a 1:1 mixture of isopropanol/water is added, and finally water is added. Once the pyrophoric material appears to have been entirely consumed, and the addition of water gives no sign of reaction, the quenching mixture should be warmed to 20 °C and stirred for at least 6 additional hours to ensure that the contents have completely reacted. The solution should be neutralized by the addition of citric or acetic acid while the mixture is still under an inert atmosphere. After the acid addition, the hydroxides formed should dissolve and the mixture should become homogenous.

Extreme caution must be exercised if the mixture is not homogenous at the end of this process, as small amounts of pyrophoric material may still be present if they are coated in a layer of oxidized material. Because of this, it is best to stir the mixture until all solids dissolve. Once the process is complete, the mixture may be disposed of as organic solvent waste. If toluene or other organic solvents have not been added to the flask, the mixture may be poured down the drain. (Note: If a mercury amalgam is quenched, the resulting waste must be treated as mercury-contaminated waste.)

*Method 2: Only suitable for small scale quenches*

It may not be possible or practical to transfer the contents to a Schlenk flask for quenching of items that have become contaminated while handling pyrophoric materials. Some examples included MeLi solution left in a syringe after use, Na powder on a frit removed from the glovebox, or alkali metals that adhere to a metal spatula. As long as the amount of pyrophoric material is small, it may be quenched by the careful addition of ice. The material should be added to a large quantity of ice. Because the ice both quenches and cools the reaction, it is advisable to add all the ice at once. When using this method, organic solvents should never be added to the quenching-mixture, as they would provide a source of flammable material that could be ignited. Once the material appears quenched, the ice bath should be allowed to melt and the contents stirred until it warms to 20 °C. The solution should be neutralized by the addition of citric or acetic acid if it is to be disposed of down the drain.

***Section 2 – Hazardous Chemicals***

* ***Organolithium reagents*** - typically in hydrocarbon solvents. Note: *tert*-butyllithium solutions are highly pyrophoric.
* ***Organomagnesium reagents*** - including Grignard reagents (RMgX) - Typically in hydrocarbon solvents. Neat reagents are pyrophoric.
* ***Organoaluminum reagents*** - Neat or in hydrocarbon solvents. Neat reagents are highly pyrophoric.
* ***Organozinc reagents*** - Neat reagents are pyrophoric.
* ***Boranes*** - Neat reagents are pyrophoric.
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* ***Group 1 metals*** – Li, Na, K

***Section 3 – Potential Hazards***

When exposed to moisture or air in an uncontrolled manner, these reagents will ignite. Such fires may be smothered with sand or extinguished with a sand fire extinguisher.

Incomplete quenching of pyrophoric materials may also result in a fire. If isopropanol has been added to the flask, even a small amount of unquenched material may be capable of igniting this solvent. As a result, it is essential that the material be completely consumed during the quenching process. This may be insured by stirring the mixture for a long time, and neutralizing the solution by the addition of acid.

***Section 4 – Approvals Required***

Lab workers should be familiar with the procedure outlined herein, as well as the properties of the specific substance to be quenched. All COSHH regulations should be complied with including supervision by supervisor or experienced researcher on first occasion.

***Section 5 – Designated Area***

The procedure should be performed in a well-ventilated fume hood. The location of the proper fire extinguishers sand should be noted before starting the procedure.

***Section 6 – Special Handling Procedures and Storage Requirements***

Process is to be performed under an atmosphere of nitrogen gas, or argon gas in the case of lithium metal.

***Section 7 – Personal Protective Equipment***

Proper laboratory clothing and eyewear. Cotton lab coats and relevant PPE.

***Section 8 – Engineering/Ventilation Controls***

Process should be performed in a well-ventilated fume hood.

***Section 9 – Spill and Accident Procedures***

If the flask breaks during the quenching procedure, the material may be collected and transferred to a Schlenk flask with an inert-gas atmosphere. To avoid spreading of the material in case this occurs, it is safest to double-contain the flask used for quenching. If the mixture ignites while it is on the bench top or in the containment flask, either sand or a powder fire extinguisher may be used to put out the fire.

***Section 10 – Waste Disposal***

The waste may be removed as organic solvent waste. If only isopropanol and water have been used (i.e., no toluene is not contained in the flask) the neutralized waste may be disposed of down the drain. Check the current safety guidelines to ensure that the spent material may be poured into the sink. For example, if mercury or other heavy toxic metals are present in the mixture, the waste must be treated appropriately.

***Section 11 - Decontamination***

The quenched material is safer to dispose of than the original pyrophoric material. Glassware used for the procedure may be washed with soap and water.

***Section 12 – Process Steps***

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| *Process Steps* | *Safety Measures* |
| Place substance under an inert atmosphere. | Use a bubbler to prevent the flask from over pressurizing. |
| Cool mixture with an external ice bath. | None. |
| Slowly add isopropanol to the mixture. | Keep the mixture cold: if the mixture becomes hot stop the addition, and wait for it to cool. |
| Cautiously add water. | Keep the mixture cold: if the mixture becomes hot stop the addition, and wait for it to cool. |
| Stir for 6 hours or longer to ensure all pyrophoric material has been quenched. | Monitor the mixture to ensure that it does not become warmer than 20 °C. |
| Add acetic or citric acid to neutralize the solution. | If unquenched material remains, it may react violently. Monitor the temperature of the mixture. |
| Remove the inert atmosphere, and dispose of waste. | Know location of fire extinguishers for use in the event that the mixture ignites. |

Alan C. Spivey 13/09/2021

***Training Documentation***

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