

**Pyrophoric Substances**

**Introduction**

Pyrophoric substances are highly reactive chemicals that can spontaneously ignite when exposed to air, examples include t-BuLi, potassium hydride (KH) and white phosphorus. In many cases they are also water sensitive and may react with water or moisture in the air to produce flammable gases such as hydrogen which may in turn ignite. The primary risk associated with pyrophoric substances is spontaneous ignition, fires and other adverse reactions are common and generally arise from the following:

* Accidental exposure of a pyrophoric substance to air either due to ingress of air into either the stock container / reaction vessel or a spillage of the pyrophoric substance.
* Accidental discharge of the pyrophoric material into a cooling bath containing a flammable solvent (e.g. dry ice / acetone) or contact with flammable solvents during cleaning or disposal.
* Accidental contact of the pyrophoric material with an oxidising agent or water.

Given the potential consequences of a fire, it is extremely important that pyrophoric substances are handled carefully by competent individuals. In general, they should be stored and handled under an inert atmosphere such as nitrogen or argon and separated from combustible materials such as organic solvents, oils, grease, paper etc. although it is worth noting that some pyrophoric substances are supplied as solutions / suspensions in flammable solvents (e.g. tBuLi is generally supplied in n-pentane).

**Note: In addition to the risk of fire it should be remembered that pyrophoric reagents can also present other hazards either due to the reagent itself or the solvent in which it is supplied. For example, white phosphorus is highly toxic as well as pyrophoric.**

**Storage and Stock Management**

Pyrophoric substances are highly reactive, and it is important that they are stored and managed appropriately to reduce the risk of fire. The following should be considered:

* Stockpiling pyrophoric reagents should be avoided and ideally only the minimum amount required should be held at any time. New bottles should only be ordered when stock levels are low or the stocks in use have begun to degrade.
* Where practical, pyrophoric reagents should be treated as a communal resource within a research group. This helps to reduce the need for multiple bottles to be in use at a time and the amount of waste generated.
* It is good practice to create an inventory of pyrophoric materials that are held in each research group and ensure this is kept up to date. When a bottle containing a pyrophoric material is opened it should be clearly marked with the date of opening and the name of a responsible person who can be contacted in the event of a problem.
* Unused or degraded stocks should be disposed of via the University’s chemical waste contractor or (for small quantities) destroyed using a suitable method as soon as they are no longer required, and the waste generated disposed of appropriately.
* Most pyrophoric substances will be provided with specific storage instructions from the supplier often requiring them to be stored in refrigerators, under mineral oil or under an inert atmosphere. These instructions should always be communicated to users and followed closely.
* Pyrophoric substances should be stored in a suitable cabinet or spark proof refrigerator separately from incompatible materials especially combustible materials (such as solvents) or oxidising agents.
* When there is a need to transfer pyrophoric reagents from one location to another a suitable bottle carrier must be used to help contain any spillages. Care should be taken to avoid transporting pyrophoric reagents in communal areas during busy periods e.g. during lecture changeovers.

**Note: Pyrophoric and water reactive substances should not be stored in the freezer (including the freezer compartment of a refrigerator) or in cooling baths at temperatures below 5°C unless specifically instructed to do so by the manufacturer or as part of an approved (and risk assessed) process.**

**Note: Unless there is a specific reason to do otherwise, pyrophoric substances should always be stored in their original container to preserve the inert atmosphere inside the container (where present) and to reduce the risk of a spillage / fire while transferring them. If a transfer is necessary, a specific risk assessment should be carried out to ensure a safe system of work is used.**

**Safe Handling**

Most accidents involving pyrophoric materials happen during handling or transfer of the substance therefore it is of paramount importance that they are treated with caution. Any process involving the use of pyrophoric substances should be subject to a robust CoSHH risk assessment before work begins. It is strongly recommended that this assessment is countersigned by a competent person. Consider the following additional precautions:

* Ensure that the user is familiar with the handling of the substance in question including methods for transferring form one container to another and the correct treatment of waste.
* Lone working should never be permitted when working with any pyrophoric material. They should not be handled out of hours and where used in reactions that proceed overnight these should be clearly marked and the local overnight experiment procedures followed.
* The correct PPE must be worn when handling pyrophoric reagents. As a minimum this should include a cotton lab coat (synthetic lab coats **must not** be used) on top of non-synthetic clothing that covers the body fully and disposable gloves. Suitable eye protection must be worn, consider the use of a face shield when transferring highly reactive pyrophoric reagents.
* Before beginning a process involving a pyrophoric material ensure that suitable fire extinguishing equipment is available e.g. fire blankets, dry powder extinguishers, sand buckets etc. You should also ensure you are familiar with emergency showers and eye wash stations in the laboratory.
* Working areas where pyrophoric reagents are to be handled should not contain significant quantities of incompatible materials e.g. flammable solvents or combustible materials.
* When working with extremely pyrophoric materials (e.g. diethylzinc, t-BuLi) consider firmly clamping the reagent bottle or reaction vessel in bucket or tray of sand while transferring the reagent.
* Where syringes are being used to transfer a pyrophoric reagent the needle and syringe should be of the luer-lock type (or equivalent) to ensure that the needle is securely locked to the syringe to prevent them from separating during use. The fit of the needle should be checked to ensure it is secure before the transfer begins.
* Using the same syringe multiple times in a row increases the risk of the syringe becoming blocked and it is usually better to select a large enough syringe to complete the transfer in one operation where practical. A cannula may be more appropriate for larger transfer operations.
* Syringes should be filled no more than half-full to reduce the risk of the plunger becoming separated from the barrel of the syringe. **This is extremely important and serious injuries and fatalities have occurred in other academic institutions when syringe barrels have been pulled free allowing the pyrophoric material to escape.**
* Wide bore needles are preferable to narrow ones as they are much less likely to become blocked. If a syringe needle becomes blocked with a substantial amount of pyrophoric material, a septum should be placed over the end and a safe means of removing the material determined. This may involve breaking the syringe under controlled conditions (specialist advice should be sought before doing so).
* Syringe needles and cannulas should be thoroughly cleaned immediately after use using an appropriate method to ensure any residual pyrophoric material is destroyed and to reduce the risk of future blockages.

**Note: Pyrophoric substances should only be handled by individuals who have been fully trained to work with them correctly and understand the risks associated with these highly reactive chemicals. Training may be carried out locally but should be formally recorded to produce a register of authorised users.**

**Note: Exercise caution when following literature procedures involving pyrophoric materials especially in cases where the procedure is old or if changes have been made to the literature process (including scaling up the process). Ensure users are familiar with relevant technical bulletins and safety information from the supplier before working with pyrophoric reagents (e.g. Aldrich Technical Bulletin AL-134).**

**Disposal of Pyrophoric Substances**

Pyrophoric material stored in bottles under an inert atmosphere tend to degrade quite rapidly as the septum in the bottle is punctured repeatedly. Other materials (e.g. metal hydrides in oil) degrade on exposure to the atmosphere when material is removed from the container. Once a pyrophoric reagent has degraded to the point where it can no longer be used or is no longer required then it should be safely disposed of.

Large quantities of material should be retained and stored safely until disposal can be arranged via the university’s approved chemical waste contractor. For **very small quantities or for residual amounts** left behind after a chemical reaction it is often better to destroy the excess material using a suitable method. The precise method used will depend on the material in question and the correct method for one substance may not be safe for another. The following should be considered:

* Where the substance is stored under an inert atmosphere in a bottle fitted with a septum the septum should be punctured using a short needle to produce a small, permanent, non-sealing hole. The reagent bottle should be placed at the back of a fume cupboard for not less than two weeks so that moist air can enter the bottle and degrade the residual material. This should only be done in a safe location away from combustible / incompatible materials such as flammable solvents. **This may not fully degrade the remaining material so caution should be exercised when proceeding with the disposal.**
* Add one or two drops of a suitable reagent (e.g. *n*-butanol for *n*-BuLi) and assess whether the reagent is no longer reactive. If this is the case, then further reagent may be added cautiously in a dropwise manner until decomposition is complete. Once this has been completed the container should be left in safe place to react for several days.
* Any containers undergoing decomposition reactions should be clearly marked and an appropriate overnight procedure followed. Contact details for a responsible person should be available to the security team in the event of an out of hours incident.
* Caution should be exercised when cleaning out any bottles used for decomposition reactions as some material may not have been fully degraded. Care should be taken to ensure this is undertaken in areas free of combustible or incompatible materials.
* The procedure and reagents used for destruction of residual material should be appropriate for the substance and must be included in your CoSHH assessment.

**Note: For residual amounts of some reagents that are supplied in mineral oil or wax (e.g. sodium / potassium hydride) it may be necessary to add a non-polar solvent such as toluene to the residue to remove any protective coating before adding the reagent used for destruction (check the correct disposal method before beginning).**

**Note: Extreme caution should be exercised when rinsing glassware used for destruction of residues with flammable solvents such as acetone which could be ignited if destruction has not been fully completed. Care should be taken to carry out procedures of this type in a safe area away from large quantities of incompatible materials and to have appropriate fire fighting equipment available.**

**Further Information**

Working with pyrophoric substances can be hazardous and the risk of fire is high if appropriate safety procedures are not put in place before work begins. It is strongly recommended that local procedures for safe handling of pyrophoric chemicals are introduced and that only authorised users are permitted to work with these materials Further information can be obtained by contacting Safety and Environmental Protection Service and by consulting the following resources:

* Gill, G.B; Whiting, D.A. *Aldrichimica Acta* **1986**, *19*, 31-41
* Aldrich Technical Bulletin AL-134

**General Office:** 0141 3305532

**Chemical Safety Adviser:**  0141 3302799

**Appendix 1: Pyrophoric / Water Reactive Substances**

The list below includes a sample of representative pyrophoric and water reactive substances and is in no way intended to be exhaustive. Most of these reagents can be handled quite safely under controlled conditions so long as an appropriate risk assessment has been completed and suitable safety precautions introduced:

* Alkali metals lithium, sodium, potassium, rubidium, caesium, NaK alloy
* Grignard reagents RMgX (R = alkyl, X = halogen)
* Metal alkyl and aryl compounds RLi, RNa, R3Al, R2Zn
* Metal carbonyl complexes Lithium carbonyl, nickel tetracarbonyl
* Finely divided metal powders Al, Ca, Co, Fe, Mg, Mn, Pd, Pt, Ti, Sn. Zn, Zr
* Metal hydrides Lithium aluminium hydride, sodium hydride, potassium hydride
* Non-metal hydrides Diethylarsine, diethyl phosphine, diborane, phosphine, arsine
* Non-metal alkyls R3B, R3P, R3As, tetramethyl silane, tributyl phosphine
* Activated copper fuel cell catalysts Cu/ZnO/Al2O3
* Hydrogenation catalysts Raney Nickel, palladium, platinum
* White / yellow phosphorus
* Uranium, neptunium, plutonium