

REACTIVES AND EXPLOSIVES: AVOIDING THE BIG BANG

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INTRODUCTION

Reactives are common place in academic and research laboratories and pilot plants. Many are used by current laboratory personnel, while some have been left by previous occupants. Reactive chemicals or mixtures have the potential to vigorously polymerize, decompose, condense, react violently with air or water, or become self-reactive due to shock, heat pressure, temperature or light. They can enter into violent reactions during which the spontaneous liberation of heat and/or gases is too rapid to be safely dissipated by the surroundings. Thus, the reaction goes out of control and one or more of the following occurs: the vessel bursts, an explosion occurs, toxic vapors are released, spontaneous ignition occurs, a flammable gas is evolved, or a similar phenomenon occurs.

Improper handling or storage of reactive chemicals can result in costly disposal, damaged equipment, injury or even death. It is prudent practice to identify what reactives are being used and/or stored and where. By identifying potential hazards, lab personnel can take the necessary actions to minimize the risks associated with reactive chemical use and storage.

It is important that laboratory personnel be educated regarding the nature and potential hazards of reactives that they work with in and around the laboratory. Laboratory workers also need to know proper handling and disposal procedures of such materials. It is equally important to be aware of the insidious hazards lurking in the forgotten or abandoned bottles in the back of laboratory cupboards or shelving. This paper will provide information to assist in identifying such materials. It will also provide some safe handling and proper disposal procedures.

AIR REACTIVES

Air reactive chemicals are those that react violently and sometimes spontaneously with air. Most reactives are also pyrophoric. Pyrophorics spontaneously burst into flames on contact with air. Not always is the flame visible.

There are some special storage and handling considerations for air reactives.

- Purchase only the amount needed.
- Limit use in an experiment to the smallest amount that will yield meaningful results.
- Do not break the seal on the container until the product is needed.
- Date the material upon opening.
- Pyrophorics and other air reactives should be stored tightly under an inert atmosphere or an inert liquid (such as nitrogen, argon, low moisture oil or kerosene).

Table 1. Air Reactive Chemicals

METALLIC DUST	Zinc, Nickel, Titanium
ALKALI METALS	Cesium, Potassium
HYDRIDES	Barium hydride, Diborane Diisobutyl aluminum hydride
OTHER CMPDS	Dimethyl Arsine, Sodium amide

- All transfers should take place under an inert atmosphere or liquid, and if available, within a glove box.

WATER REACTIVES

Water reactive materials react with water, water vapor, or moist air to produce a flammable or toxic gas or other hazardous condition such as a fire or explosion.

Special storage and handling considerations for water reactives are as follows:

- Purchase only the amount needed.
- Date container upon opening.
- Store in a cool, dry area.
- Isolate from other reactives.
- Isolate from aqueous acids and bases.
- Properly desiccate whenever possible.
- In case of fire, a class D fire extinguisher, dry sand or soda ash should be used.

Table 2. Water Reactive Compounds

ALKALI METALS	Lithium, Sodium
HALIDES	Titanium tetrachloride, Acetyl Chloride
HYDRIDES	Diborane, Sodium hydride
OXIDES	Sodium oxide
CARBIDES	Calcium carbide
ANHYDRIDES	Acetic anhydride
PHOSPHIDES	Aluminum phosphide
OTHER HYDROLYZABLE COMPOUNDS	Chlorosulfonic acid Aluminum tribromide

PEROXIDE HAZARDS

Several common laboratory chemicals react with air to form peroxides. A single opening of a container can allow peroxide formation. These peroxides are less volatile than the solvent and tend to concentrate during distillation. When heat is applied to a crystal or concentrated solution of the peroxide it can trigger an explosive decomposition. These chemicals should never be allowed to evaporate to dryness. Other chemicals, such as butadiene, are polymerizable and can initiate a runaway explosive polymerization reaction.

Guidelines for storing and handling organic peroxides and peroxide forming compounds include the following:

- Purchase only the amount needed.
- Label bottle as possible peroxide or peroxide former.
- Date container when received/opened.
- Do not break seal on the container until the chemical is needed.
- Flush air out of free space, if possible, and maintain an inert atmosphere (nitrogen, argon) in the free space.
- Keep tightly sealed.
- Use plastic closures to reduce corrosion and friction.
- If it won't compromise the usefulness of the compound, add 0.001-0.01% inhibitor, such as hydroquinone, 4-tertiary-butylcatechol (TBC) or 2,6-di-tertiary-p-methylphenol (BHT). Consult with material safety data sheet from the manufacturer for the recommended inhibitor and procedure for adding.

- When distilling peroxidizable chemicals:
 - Test material for peroxides prior to distillation or in reactions sensitive to peroxide catalysis.
 - Add inert but miscible high boiling point substance (such as mineral oil) to prevent peroxides from concentration.
- DO NOT TEST if peroxidation is visible (crystalline solids on the bottom, around the cap, or if the liquid appears cloudy and viscous or discoloration of peroxidizable solid.)

Table 3. Organic Peroxides/ Peroxidizable

Compounds

- Any peroxide formers should NOT be opened at all if:
 - The age of the container is unknown
 - Physical characteristics do not match those of the pure substance.
- Use plastic or ceramic spatulas. Do not use metal spatulas as the metal contamination can cause explosive decomposition.
- Do not return unused peroxides back to container. Dispose as hazardous waste.
- Store organic peroxides at the lowest temperature possible consistent with the solubility or freezing point.
- Do not store at a temperature lower than the freezing point or point of precipitation. Peroxides are extremely susceptible to shock and heat during phase changes.
- Do not trust expiration date as the absence of peroxides.

PEROXIDE HAZARD ON STORAGE HIGHLY HAZARDOUS IN 3 MONTHS	
Divinyl acetylene	Isopropyl ether
Sodium amide	Vinylidene Chloride
Potassium amide	Potassium metal
PEROXIDE HAZARD ON CONCENTRATION STORE LESS THAN 1 YEAR	
Acetal	Cyclohexene
Decalin	Methylacetylene
2- Propanol	Tetrahydrofuran
Dioxane	Vinyl ether
Diethyl ether	
Dicyclopentadiene	
Ethylene glycol dimethyl ether (GLYME)	
Furan	
PEROXIDE INITIATED POLYMERIZATION STORE LESS THAN 1 YEAR	
Acrylic acid	Vinyl pyridine
Acrylonitrile	Styrene
Butadiene	
Tetrafluoroethylene	

SHOCK SENSITIVE AND EXPLOSIVE MATERIALS

Shock sensitive and explosive chemicals can spontaneously release large quantities of energy under ambient conditions or when subjected to shock through bumping, friction, heat or agitation. The energy release can be thermal or physical. Some shock sensitive chemicals are explosive because they can yield a deflagration (characteristic of a low explosive giving a very rapid auto-combustion of particles) or a detonation (extremely rapid decomposition accompanied by high-pressure-temperature a wave that moves at 1000-9000 meters per second). When such an event occurs unexpectedly or in an uncontrolled fashion, the results can be serious bodily injury or extensive damage to property.

“Nitro” compounds (nitrated organics and inorganics) constitute the largest class of chemical substances that are known for their explosive characteristics. Organic nitro explosives can be classified in two categories: (1) nitro-substituted hydrocarbons (e.g., nitromethane,

trinitrobenzene and trinitrotoluene) and (2) nitrate esters (e.g., Nitroglycerine and ethylene glycol dinitrate). Picric acid is a “trinitro” compound that hydrated with $\geq 10\%$ water is considered a flammable solid. It becomes a powerful explosive when dry.

Recommended storage and safe handling procedures for shock sensitive and explosive material are as follows:

- Purchase only the amount needed.
- When receiving or using any new product, review safety data.
- Date chemical when received/opened.
- DO NOT open or handle if product appears to have dried out completely.
- If an explosive reaction is possible, conduct the operation behind shielding.
- Visually inspect container on a periodic basis.
- If appropriate, add water as needed to avoid dryness.
- Precautions for perchlorates and perchloric acid use:
 - Perchloric acid should be used in a water wash down hood.
 - Digest organic material in nitric acid prior to adding perchloric acid.
 - Perchlorate esters can act like nitroglycerine.
 - Do not use perchloric acid around wooden furniture.
 - Do not mix perchloric acid with sulfuric acid as anhydrous perchloric acid can form.
 - Store perchloric acid containers in glass or ceramic trays.

Guidelines for reaction operations are as follows:

- Use heating tapes, mantels or sand, water or oil baths.
- Do not use heat guns or opened coiled hot plates if flammable vapors are present.
- Do not use oil baths if oxidizing agents are present.
- Keep controls for heat and stirrers outside shielding if possible.
- Change oil once a month in pumps if exposed to reactive gases.
- Use tygon, rubber or copper tubing (choose appropriate material for specific reaction) for vent lines.

Table 4. Shock Sensitive and Explosive Compounds

ACETYLENIC COMPOUNDS	
Acetylene	Copper Acetalide
Ethoxyacetylene	Propyne
Propyne peroxide	Disilver acetylide
AZIDES	
Silver azide	Lead(II) azide
Carbonyl diazide	
AZO COMPOUNDS	
Diazirine	Azomethane
Diazomethane	
FULMINATES	
Silver fulminate (from Tollen's Reagent)	
Sodium fulminate	Mercury fulminate
CHLORITE/CHLORATE/ PRECHLORATE/IODATES	
Sodium chlorite	Lead tetrachloride
Silver chlorate	Lead perchlorate
ORGANIC PEROXIDES	
Peracetic acid	Benzoyl peroxide
NITRATE AND NITRITE AMIDES	
N-Nitroso-N-methyl urea	
METAL PICRATES	
Lead picrate	Nickel picrate
NITRO COMPOUNDS/ NITRATE ESTERS	
Nitromethane	Nitrocellulose
Nitroglycerine	Trinitrotoluene
Silver amide	Silver nitride
Nitrocyanide	Disulfur dinitride
Dinitrophenol	Dinitrobenzene

- Vent all pumps to hood or trap.
- Support tubing and vent lines so they do not sag.
- Wear proper personal protective equipment:
 - Goggles/Face shield
 - Heavy leather or lineman gloves should be worn when reaching behind shielded area.
 - Laboratory coat made of slow burning material and quick release fasteners.
 - Use tongs or remote control equipment to manipulate highly reactive chemicals whenever possible to minimize exposure to any part of the body.

If a runaway reaction occurs while working with a reactive material:

- Remove any heat source.
- Cool the batch.
- Stop adding any reagents to the reaction process.
- Alert others in the area.
- Close the hood.
- Move away from the reaction until the temperature has dropped.

DISPOSAL OF REACTIVES

It is important to dispose of reactive and explosive chemicals properly. There are safe methods to reduce the hazardous characteristics of many reactive chemicals in the laboratory. While deactivation and neutralization methods are available, such “treatment” may not be permitted under the Resource, Conservation and Recovery Act (RCRA) unless done as the final step in the reaction process within the laboratory. If treatment cannot take place in the lab or the institutional waste facility due to permit restrictions, the only option may be contracting a commercial vendor to handle the reactive chemical waste. This can be extremely costly. Some of the costs can be limited by knowing how the vendor will require packaging of the waste. That information will have an impact on how the waste is collected in the laboratory. Pre-experiment planning can be beneficial in accomplishing a safe and economical transfer to a commercial vendor.

For those institutions with Part B permit for a treatment, storage and disposal facility (TSDF), many of the treatment or deactivation procedures can be carried out at the waste facility rather than in the laboratory itself. It is imperative that laboratory personnel follow their institution’s waste disposal guidelines in accordance to local, state, and federal regulations.

SUMMARY

Several tables have been included which identify reactive classes with specific examples to assist in determining what reactives may exist in a lab. These lists are not all inclusive and they do not eliminate the responsibility for reactive chemical users to read the Material Safety Data Sheet (MSDS) and other available literature on the recommended handling procedures.

While many laboratory workers find that alphabetical storage of chemicals promotes ease in locating, this is very dangerous. Chemicals should be stored according to hazard class and compatibility.

To minimize the potential of reactive and explosives sneaking up on an unsuspecting worker, researchers should be encouraged to review their inventory periodically and dispose of chemicals that are outdated or in containers whose integrity has been challenged. Also, when researchers leave the institution, removal of chemicals and/or waste should take place prior to the researcher's departure. This provides the opportunity to identify "unlabeled" containers and ascertain any information needed for proper disposal.

Though there are risks associated with the use of reactive chemicals, identification, education, minimization of stock, and proper and timely disposal can significantly reduce the hazards, thus making the laboratory a safer place.

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