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Guidance for Reactive and Peroxide Forming Chemicals

Foreword:

This document provides supplementary guidance for the handling and testing of reactive and peroxide forming chemicals. This information was taken directly from the book “Prudent Practices in the Laboratory” verbatim and edited/abbreviated for readability and brevity. Additional guidance pertaining to testing, safe storage and time limits was obtained from a written document by the Hazards Control Department at the Lawrence Livermore National Laboratory. Basic information on the hazards associated with various kinds of reactive chemicals is included along with a list of chemicals that require special attention on pages 6-11. This document does not replace detailed information that can be found within a chemicals safety data sheet and standard operating procedures involving the use of a chemical. This information should be provided for staff and may be kept either as a separate document or incorporated into a department’s chemical hygiene plan.

Always refer to a chemicals safety data sheet and supplier instructions for the proper use and storage of reactive and peroxide forming chemicals!

Water Reactives:

Water-reactive materials are those that react violently with water. Alkali metals (e.g., lithium, sodium, and potassium), many organometallic compounds, and some hydrides react with water to produce heat and flammable hydrogen gas, which ignites or combines explosively with atmospheric oxygen. Some anhydrous metal halides (e.g., aluminum bromide), oxides (e.g., calcium oxide), nonmetal oxides (e.g., sulfur trioxide), and halides (e.g., phosphorus pentachloride) react exothermically with water, resulting in a violent reaction if there is insufficient coolant water to dissipate the heat produced.



Pyrophorics:

For pyrophoric materials, oxidation of the compound by oxygen or moisture in air proceeds so rapidly that ignition occurs. Many finely divided metals are pyrophoric, and their degree of reactivity depends on particle size, as well as factors such as the presence of moisture and the thermodynamics of metal oxide or metal nitride formation. Other reducing agents, such as metal hydrides, alloys of reactive metals, low-valent metal salts, and iron sulfides, are also pyrophoric.



Explosives:

An explosive is any chemical compound or mechanical mixture that, when subjected to heat, impact, friction, detonation, or other suitable initiation, undergoes rapid chemical change, evolving large volumes of gases that exert pressure on the surrounding medium. The term applies to materials that either detonate or deflagrate. Heat, light, mechanical shock, and certain catalysts initiate explosive reactions. Hydrogen and chlorine react explosively in the presence of light. Acids, bases, and other substances catalyze the explosive polymerization of acrolein, and many metal ions can catalyze the violent decomposition of hydrogen peroxide. Shock-sensitive materials include acetylides, azides, nitrogen triiodide, organic nitrates, nitro compounds, perchlorate salts (especially those of heavy metals such as ruthenium and osmium), many organic peroxides, and compounds containing diazo, halamine, nitroso, and ozonide functional groups. See appendix A for a list of functional groups found in some explosive compounds.



Organic Peroxides

Organic peroxides are a special class of compounds with unusually low stability that makes them among the most hazardous substances commonly handled in laboratories, especially as initiators for free-radical reactions. Although they are low-power explosives, they are hazardous because of their extreme sensitivity to shock, sparks, and other forms of accidental detonation. Many peroxides that are used routinely in laboratories are far more sensitive to shock than most primary explosives (e.g., TNT), although many have been stabilized by the addition of compounds that inhibit reaction. Nevertheless, even low rates of decomposition may automatically accelerate and cause a violent explosion, especially in bulk quantities of peroxides (e.g., benzoyl peroxide). These compounds are sensitive to heat, friction, impact, and light, as well as to strong oxidizing and reducing agents. All organic peroxides are highly flammable, and fires involving bulk quantities of peroxides should be approached with extreme caution.



Oxidizers:

Oxidizing agents may react violently when they come into contact with reducing materials and sometimes with ordinary combustibles. Such oxidizing agents include halogens, chromates, and functional groups with additional oxygen in their formula indicated by the use of the prefix “per” in the compounds name. Perchloric acid is a powerful oxidizing agent with organic compounds and other reducing agents. Perchlorate salts are explosive and should be treated as potentially hazardous compounds. Some common oxidants are as follows:

- **Gases:** chlorine, fluorine, nitrous oxide, oxygen, ozone, steam
- **Liquids:** bromide, hydrogen peroxide, nitric acid, perchloric acid, sulfuric acid
- **Solids:** bromates, chlorates, chlorites, chromates, dichromates, hypochlorites, iodates, nitrates, nitrites, perchlorates, persulfates, peroxides, permanganates, picrates

Peroxidizables:

Certain common laboratory chemicals form peroxides on exposure to oxygen in air. Over time, some chemicals continue to build peroxides to potentially dangerous levels, whereas others accumulate a relatively low equilibrium concentration of peroxide, which becomes dangerous only after being concentrated by evaporation or distillation. The peroxide becomes concentrated (application of heat and subsequent evaporation) because it is less volatile than the parent chemical. A related class of compounds includes inhibitor-free monomers (a monomer is a basic chemical unit/molecule that makes up a polymer; example: glucose is a monomer of cellulose) prone to free radical polymerization that on exposure to air can form peroxides or other free radical sources capable of initiating violent polymerization. Note that care must be taken when storing and using these monomers - most of the inhibitors used to stabilize these compounds require the presence of oxygen to function properly. Excluding oxygen by storing potential peroxide formers under an inert atmosphere (N₂ or argon) greatly increases their safe storage lifetime. Purchasing the chemical stored under nitrogen in septum-capped bottles is also possible. In some cases, stabilizers or inhibitors (free-radical scavengers that terminate the chain reaction) are added to the liquid to extend its storage lifetime. Because distillation of the stabilized liquid removes the stabilizer, the distillate must be stored with care and monitored for peroxide formation.

Precautions for handling peroxides:

- Limit the quantity of peroxide forming chemicals to the minimum amount required. Do not return unused quantities to the original container. All inventories should be kept to a minimum and managed on a first in-first out basis.

- Clean up all spills immediately. Solutions of peroxides can be absorbed on vermiculite or other absorbing material. Contact SEM at 581-4055 to pick up spill material.
- Reduce the sensitivity of most peroxides to shock and heat by dilution with inert solvents, such as aliphatic hydrocarbons (straight chained, single or double bonded C-H compounds). However, do not use aromatics (such as toluene), which are known to induce the decomposition of diacyl peroxides.
- Do not use solutions of peroxides in volatile solvents under conditions in which the solvent might vaporize because this will increase the peroxide concentration in the solution.
- Do not use metal spatulas to handle peroxides because contamination by metals can lead to explosive decomposition. Magnetic stirring bars can unintentionally introduce iron, which can initiate an explosive reaction of peroxides. Ceramic, Teflon, or wooden spatulas and stirring blades may be used if it is known that the material is not shock sensitive.
- Do not permit open flames and other sources of heat near peroxides. It is important to label areas that contain peroxides so that this hazard is evident.
- Avoid friction, grinding, and all forms of impact near peroxides, especially solid peroxides. Glass containers that have screw-cap lids or glass stoppers should not be used. Polyethylene bottles that have screw-cap lids may be used.
- To minimize the rate of decomposition, store peroxides at the lowest possible temperature consistent with their solubility or freezing point. Do not store liquid peroxides or solutions at or lower than the temperature at which the peroxide freezes or precipitates because peroxides in these forms are extremely sensitive to shock and heat.
- If possible (transparent containers), visually check the consistency of any liquids. Arrange for the disposal of any chemicals that are suspected show evidence of peroxide formation either from the precipitation of crystals or the appearance of “strings” with in the homogeneity of the solution.
- Do not attempt to open peroxide forming chemicals beyond their expiration dates! Some compounds can be deadly when peroxidized, and the act of unscrewing a cap or dropping a bottle can be enough to trigger an explosion. Contact SEM immediately for collection and disposal.

Labeling and Testing

All bottles of peroxide forming chemicals should be dated with the date they are opened. Peroxide test strips are relatively inexpensive and may be purchased from a number of vendors online. Test strips purchased should be low range (E.g. 0-25ppm). When tested, the date of test and the results should also be written on bottle. Alternatively tape or a premade label may be used so long as it doesn't interfere with the bottles primary label. Chemicals that show evidence of peroxide formers should be closely monitored. Arrangements for disposal should be made for chemicals with test results approaching 10ppm or greater. Bottles should be disposed of in a timely manner by either the guidance listed in the tables below or by the expiration date on the containers label. Please notify SEM of the test results when arrangements for pick up and disposal are made.

Peroxide Classes: A, B, C

Class A compounds are especially dangerous when peroxidized and should not be stored for long periods in the laboratory. Good practice requires they be discarded within 3 months of receipt. Testing is not recommended. If a container of a Class A peroxidizable is past its expiration date, or if the presence of peroxides is suspected or proven, do not attempt to open the container!

| |
|--|
| Class A: Chemicals that form explosive levels of peroxides without concentration – Discard within 3 months |
| Isopropyl ether |
| Butadiene |
| Chlorobutadiene (chloroprene) |
| Potassium amide |
| Potassium metal |
| Sodium amide (sodamide) |
| Tetrafluoroethylene |
| Divinyl acetylene |
| Vinylidene chloride |

Class B materials are often sold with autoxidation inhibitors. If the inhibitor is removed, or if inhibitor-free material is purchased, particular care must be taken in their long-term storage because of the enhanced probability of peroxide formation. Purging the container headspace with nitrogen is recommended. No special disposal precautions are required for peroxide-contaminated Class B materials.

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| Class B: Chemicals forming peroxide hazards on concentration. Class B materials should be stored in a dark location. If stored in glass bottles, the glass should be amber. Containers should be marked with their opening date and inspected/tested every 6 months thereafter. Discard after 12 months. |
| Acetal |
| Cumene |
| Cyclohexene |
| Cyclooctene |
| Cyclopentene |
| Diacetylene |
| Dicyclopentadiene |
| Diethylene glycol dimethyl ether (diglyme) |
| Diethyl ether |
| Dioxane (p-dioxane) |
| Ethylene glycol dimethyl ether (glyme) |
| Furan |
| Methyl acetylene |
| Methyl cyclopentane |
| Methyl-isobutyl ketone |
| Tetrahydrofuran |
| Tetrahydronaphthalene |
| Vinyl ethers |

In most cases, commercial samples of **Class C materials** are provided with polymerization inhibitors that require the presence of oxygen to function and therefore are not to be stored under inert atmosphere. Inhibitor-free samples of Class C compounds (i.e., the compound has been synthesized in the laboratory or the inhibitor has been removed from the commercial sample)

should be kept in the smallest quantities required and under inert atmosphere. Unused material should be properly disposed of immediately, or if long-term storage is necessary, an appropriate inhibitor should be added.

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| Class C: Unsaturated monomers that may autopolymerize as a result of peroxide accumulation if inhibitors have been removed or are depleted. Class C materials should be stored in a dark location. If stored in glass bottles, the glass should be amber. Containers should be marked with their opening date and inspected every 6 months thereafter. Without inhibitor, chemicals should be used within 5 days upon receipt and discarded within 24 hours upon opening. Inhibitor added - Discard after 12 months |
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|--------------|
| Acrylic acid |
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|-----------|
| Butadiene |
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|-------------------------|
| Chlorotrifluoroethylene |
|-------------------------|

| |
|----------------|
| Ethyl acrylate |
|----------------|

| |
|---------------------|
| Methyl methacrylate |
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|---------|
| Styrene |
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|---------------|
| Vinyl acetate |
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|----------------|
| Vinyl chloride |
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|----------------|
| Vinyl pyridine |
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Determining Reaction Quantities

When a possibly hazardous reaction is attempted, small quantities of reactants should be used. When handling highly reactive chemicals, use the smallest quantities needed for the experiment. In conventional explosives laboratories, no more than 0.1 g of product should be prepared in a single run. During the actual reaction period, no more than 0.5 g of reactants should be present in the reaction vessel: The diluent, the substrate, and the energetic reactant must all be considered when determining the total explosive power of the reaction mixture. Special formal risk assessments should be established to examine operational and safety problems involved in scaling up a reaction in which an explosive substance is used or could be generated.

Conducting Reaction Operations

The most common heating devices are heating tapes and mantles and sand, water, steam, wax, silicone oil, and air (or nitrogen) baths. They should be used in such a way that if an explosion were to occur the heating medium would be contained. Heating baths should consist of nonflammable materials. All controls for heating and stirring equipment should be operable from outside the shielded area. Vacuum pumps should carry tags indicating the date of the most recent oil change. Oil should be changed once a month, or sooner if it is known that the oil has been unintentionally exposed to reactive gases. All pumps should be either vented into a hood or trapped. Vent lines may be Tygon, rubber, or copper. If Tygon or rubber lines are used, they should be supported so that they do not sag and cause a trap for condensed liquids.

Materials Requiring Special Attention:

The following list is not intended to be all-inclusive:

Acetylenic compounds, both organic and inorganic (especially heavy metal salts), can be explosive and shock sensitive. At pressures of 2 atm or greater and moderate temperature, acetylene (C₂H₂)

has been reported to decompose explosively, even in the absence of air. Because of these dangers, acetylene must be handled in acetone solution and never stored alone in a cylinder.

Alkyl lithium compounds are highly reactive and pyrophoric. Violent reactions may occur on exposure to water, carbon dioxide, and other materials. They are also highly corrosive to the skin and eyes. Tert-Butyllithium solutions are the most pyrophoric and may ignite spontaneously on exposure to air. Contact with water or moist materials can lead to fires and explosions. These compounds should be stored and handled under an inert atmosphere in areas that are free from ignition sources.

Aluminum chloride (AlCl₃) should be considered a potentially dangerous material. If moisture is present, sufficient decomposition may form hydrogen chloride (HCl) and build up considerable pressure. If a bottle is to be opened after long storage, it should first be completely enclosed in a heavy towel.

Ammonia and amines. Ammonia (NH₃) reacts with iodine to give nitrogen triiodide, which explodes on touch. Ammonia reacts with hypochlorites (bleach) to give chlorine. Mixtures of ammonia and organic halides sometimes react violently when heated under pressure. Ammonia is combustible. Inhalation of concentrated fumes can be fatal. Ammonia and amines can react with heavy metal salts to produce explosive fulminates.

Azides, both organic and inorganic, and some azo compounds can be heat and shock sensitive. Azides such as sodium azide can displace halide from chlorinated hydrocarbons such as dichloromethane to form highly explosive organic polyazides; this substitution reaction is facilitated in solvents such as dimethyl sulfoxide.

Boron trifluoride and boron trichloride (BF₃ and BCl₃, respectively) react with water to give HF and HCl, respectively. Their fumes are corrosive, toxic, and irritating to the eyes and mucous membranes.

Carbon disulfide (CS₂) is both very toxic and very flammable; mixed with air, its vapors can be ignited by a steam bath or pipe, a hot plate, or a lightbulb.

Chlorine (Cl₂) is highly toxic and may react violently with hydrogen (H₂) or with hydrocarbons when exposed to sunlight.

Chlorine trifluoride (ClF₃) in liquid form is corrosive and very toxic. It is a potential source of explosion and causes deep penetrating burns on contact with the body. The effect may be delayed and progressive, as in the case of burns caused by hydrogen fluoride. Chlorine trifluoride reacts vigorously with water and most oxidizable substances at room temperature, frequently with immediate ignition. It reacts with most metals and metal oxides at elevated temperatures. In addition, it reacts with silicon-containing compounds and thus can support the continued combustion of glass, asbestos, and other such materials. Chlorine trifluoride forms explosive mixtures with water vapor, ammonia, hydrogen, and most organic vapors.

Diazomethane (CH₂N₂) and related diazo compounds should be treated with extreme caution. They are very toxic, and the pure gases and liquids explode readily even from contact with sharp edges of glass. Solutions in ether are safer from this standpoint. An ether solution of diazomethane is rendered harmless by dropwise addition of acetic acid.

Diethyl and other ethers, including tetrahydrofuran and 1,4-dioxane and particularly the branched-chain type of ethers, may contain peroxides that have developed from air autoxidation. Concentration of these peroxides during distillation may lead to explosion. Ferrous salts or sodium bisulfite can be used to decompose these peroxides, and passage over basic active alumina can remove most of the peroxidic material. In general, however, dispose of old samples of ethers if they test positive test for peroxide.

Diisopropyl ether is a notoriously dangerous, Class A peroxide former. The peroxide is not completely soluble in the mother liquor. Peroxide concentrations from autoxidation may form saturated solutions that then crystallize the peroxide as it is being formed. There are numerous reports of old bottles of diisopropyl ether being found with large masses of crystals settled at the bottom of the bottle. These crystals are extremely shock sensitive, even while wetted with the diisopropyl ether supernatant. Mild shock (e.g., bottle breakage, removing the bottle cap) is sufficient to result in explosion. This ether should not be stored in the laboratory. Only the amount required for a particular experiment or process should be purchased; any leftover material should be disposed of immediately.

Dimethyl sulfoxide (DMSO), (CH₃)₂SO, decomposes violently on contact with a wide variety of active halogen compounds, such as acyl chlorides. Explosions from contact with active metal hydrides have been reported. DMSO does penetrate and carry dissolved substances through the skin membrane.

Dry benzoyl peroxide (C₆H₅CO₂)₂ is easily ignited and sensitive to shock. It decomposes spontaneously at temperatures greater than 50 °C. It is reported to be desensitized by addition of 20% water.

Dusts that are suspensions of oxidizable particles (e.g., magnesium powder, zinc dust, carbon powder, and flowers of sulfur) in the air can constitute powerful explosive mixtures. These materials should be used with adequate ventilation and should not be exposed to ignition sources. When finely divided, some solids, including zirconium, titanium, Raney nickel, lead (such as prepared by pyrolysis of lead tartrate), and catalysts (such as activated carbon containing active metals and hydrogen), can combust spontaneously if allowed to dry while exposed to air and should be handled wet.

Ethylene oxide (C₂H₄O) has been known to explode when heated in a closed vessel. Experiments using ethylene oxide under pressure should be carried out behind suitable barricades.

Fluorine (F₂) is an extremely toxic reactive oxidizing gas with extremely low permissible exposure levels. Only trained personnel should be authorized to work with fluorine. (See Vignette 6.4.) Anyone planning to work with fluorine must be knowledgeable of proper first-aid treatment and have the necessary supplies on hand before beginning.

Halogenated compounds, such as chloroform (CHCl₃), carbon tetrachloride (CCl₄), and other halogenated solvents, should not be dried with sodium, potassium, or other active metals; violent explosions usually result. Many halogenated compounds are toxic. Oxidized halogen compounds—chlorates, chlorites, bromates, and iodates—and the corresponding peroxy compounds may be explosive at high temperatures.

Hydrogen fluoride and hydrogen fluoride generators. Anhydrous HF or hydrogen fluoride is a colorless liquid that boils at 19.5 °C. It has a pungent irritating odor, and a time-weighted average exposure of 3 ppm for routine work. Aqueous HF is a colorless very corrosive liquid that fumes at concentrations greater than 48%. It attacks glass, concrete, and some metals, especially cast iron and alloys containing silica as well as organic materials such as leather, natural rubber, wood, and human tissue. Although HF is nonflammable, its corrosive action on metals can result in the formation of hydrogen in containers and piping, creating a fire and explosion hazard. HF should be stored in tightly closed polyethylene containers. HF attacks glass and therefore should never be stored in a glass container. HF causes severe injury via skin and eye contact, inhalation, and ingestion. It is very aggressive physiologically because the fluoride ion readily penetrates the skin and may cause decalcification of the bones and systemic toxicity, including pulmonary edema, cardiac arrhythmia and death. Burns from HF may not be painful or visible for several hours and even moderate exposure to concentrated HF can result in fatality.

Hydrogen peroxide (H₂O₂) stronger than 3% can be dangerous; in contact with skin, it causes severe burns. Thirty percent H₂O₂ may decompose violently if contaminated with iron, copper, chromium, or other metals or their salts. Stirring bars may inadvertently bring metal into a reaction and should be used with caution.

Hydrogen selenide (H₂Se) is a colorless gas with an offensive odor. It is a dangerous fire and explosion risk and reacts violently with oxidizing materials. Hydrogen selenide is an irritant to eyes, mucous membranes, and the pulmonary system. Acute exposures can cause symptoms such as pulmonary edema, severe bronchitis, and bronchial pneumonia. Symptoms also include gastrointestinal distress, dizziness, increased fatigue, and a metallic taste in the mouth.

Hydrogen sulfide (H₂S) is a highly toxic and flammable gas. Although it has a characteristic odor of rotten eggs, it fatigues the sense of smell. This could result in failure to notice the seriousness of the situation before health becomes at risk and is problematic for rescuers who think danger has passed when the odor disappears.

Liquid nitrogen—cooled traps open to the atmosphere condense liquid air rapidly. When the coolant is removed, an explosive pressure buildup occurs, usually with enough force to shatter glass equipment if the system has been closed. Hence, only sealed or evacuated equipment should be so cooled. Vacuum traps must not be left under static vacuum; liquid nitrogen in Dewar flasks must be removed from these traps when the vacuum pumps are turned off.

Lithium aluminum hydride (LiAlH₄) should not be used as a drying agent for solvents that are hygroscopic and may contain high concentrations of water, such as methyl ethers and tetrahydrofuran; fires from reaction with damp ethers are often observed. Predrying these solvents with a less efficient drying agent, followed by LiAlH₄ treatment is recommended. The reaction of LiAlH₄ with carbon dioxide has reportedly generated explosive products. Carbon dioxide or bicarbonate extinguishers should not be used for LiAlH₄ fires; instead, such fires should be smothered with sand or some other inert substance.

Methyl chloride (CH₃Cl) has a slight, not unpleasant, odor that is not irritating and may pass unnoticed unless a warning agent has been added. Exposure to excessive concentrations is indicated by symptoms similar to those of alcohol intoxication, that is, drowsiness, mental confusion, nausea, and possibly vomiting. Methyl chloride may, under certain conditions, react with aluminum or

magnesium to form materials that ignite or fume spontaneously with air, and contact with these metals should be avoided.

Nitric acid is a strong acid, very corrosive, and decomposes to produce nitrogen oxides. The fumes are very irritating, and inhalation may cause pulmonary edema. Nitric acid is also a powerful oxidant and reacts violently, sometimes explosively reducing agents (e.g., organic compounds) with liberation of toxic nitrogen oxides. Contact with organic matter must be avoided. Extreme caution must be taken when cleaning glassware contaminated with organic solvents or material with nitric acid. Toxic fumes of NO_x are generated and explosion may occur.

Nitrate, nitro, and nitroso compounds may be explosive, especially if more than one of these groups is present in the molecule. Alcohols and polyols may form highly explosive nitrate esters (e.g., nitroglycerine) from reaction with nitric acid.

Organometallics may be hazardous because some organometallic compounds burn vigorously on contact with air or moisture. For example, solutions of tert-Butyllithium ignite some organic solvents on exposure to air. The pertinent information should be obtained for a specific compound.

Oxygen tanks should be handled with care because serious explosions have resulted from contact between oil and high-pressure oxygen. Oil or grease should not be used on connections to an O₂ cylinder or gas line carrying O₂.

Ozone (O₃) is a highly reactive toxic gas. It is formed by the action of ultraviolet light on oxygen (air), and therefore certain ultraviolet sources may require venting to the exhaust hood. Ozonides can be explosive.

Palladium (Pd) or platinum (Pt) on carbon, platinum oxide, Raney nickel, and other catalysts presents the danger of explosion if additional catalyst is added to a flask in which an air-flammable vapor mixture or hydrogen is present. The use of flammable filter paper should be avoided.

Perchlorates should be avoided whenever possible. Perchlorate salts of organic, organometallic, and inorganic cations are potentially explosive and may detonate by heat or shock. Whenever possible, perchlorate should be replaced with safer anions such as fluoroborate, fluorophosphates, and trifluoromethanesulfonate (triflate). Special HClO₄ hoods are available from many manufacturers. Disassembly of such chemical hoods must be preceded by washing the ventilation system to remove deposited perchlorates.

Permanganates are explosive when treated with sulfuric acid. If both compounds are used in an absorption train, an empty trap should be placed between them and monitored for entrapment.

Peroxides (inorganic) should be handled carefully. When mixed with combustible materials, barium, sodium, and potassium peroxides form explosives that ignite easily.

Phenol is a corrosive and moderately toxic substance that affects the central nervous system and can cause damage to the liver and kidneys. Phenol-formaldehyde reactions are used in creation of phenolic resins, and can be highly exothermic. These reactions have been implicated in a number of plant-scale accidents when runaway reactions caused a sudden rise in pressure and rupturing of pressure disks or vessels. Care should be taken if performing such reactions in the laboratory.

Phosphine (PH₃) is a spontaneously flammable and explosive poisonous colorless gas with the foul odor of decaying fish. The liquid can cause frostbite. Phosphine is a dangerous fire hazard and ignites in the presence of air and oxidizers. It reacts with water, acids, and halogens. If heated, it forms hydrogen phosphides, which are explosive and toxic. There may be a delay between exposure and the appearance of symptoms.

Phosphorus (P) (red and white) forms explosive mixtures with oxidizing agents. White phosphorus should be stored underwater because it ignites spontaneously in air. The reaction of phosphorus with aqueous hydroxides gives phosphine, which is toxic and also may either ignite spontaneously or explode in air.

Phosphorus trichloride (PCl₃) reacts with water to form phosphorous acid with HCl evolution; the phosphorous acid decomposes on heating to form phosphine, which may either ignite spontaneously or explode. Care should be taken in opening containers of PCl₃, and samples that have been exposed to moisture should not be heated without adequate shielding to protect the operator.

Piranha solution is a mixture of concentrated sulfuric acid and 30% hydrogen peroxide. It is a powerful oxidant and strong acid used to remove organic residues from various surfaces. Many instances of explosions have been reported with this solution upon contact with reducing agents, especially organics. The solution slowly evolves oxygen, and therefore containers must be vented at all times.

Potassium (K) is much more reactive than sodium; it ignites quickly on exposure to humid air, and therefore should be handled under the surface of a hydrocarbon solvent such as mineral oil or toluene. Potassium can form a crust of the superoxide (KO₂) or the hydrated hydroxide (KOH·H₂O) on contact with air. If this happens, the act of cutting a surface crust off the metal or of melting the encrusted metal can cause a severe explosion due to oxidation of the organic oil or solvent by superoxide, or from reaction of the potassium with water liberated from the hydrated hydroxide.

Silane (SiH₄) is a pyrophoric colorless gas that ignites spontaneously in air. It is incompatible with water, bases, oxidizers, and halogens. The gas has a choking repulsive odor. Silyl halides are toxic colorless gases with a pungent odor. They are corrosive irritants to the skin, eyes, and mucous membranes. When silyl halides are heated, toxic fumes can be emitted.

Sodium (Na) should be stored in a closed container under kerosene, toluene, or mineral oil. Scraps of sodium or potassium should be destroyed by reaction with n-butyl alcohol. Contact with water should be avoided because sodium reacts violently with water to form hydrogen (H₂) with evolution of sufficient heat to cause ignition. Carbon dioxide, bicarbonate, and carbon tetrachloride fire extinguishers should not be used on alkali metal fires.

Sodium amide (NaNH₂) can undergo oxidation on exposure to air to give sodium nitrite in a mixture that is unstable and may explode.

Sulfuric acid (H₂SO₄) should be avoided, if possible, as a drying agent in desiccators. If it must be used, glass beads should be placed in it to help prevent splashing when the desiccator is moved. To

dilute H₂SO₄, the acid should be added slowly to cold water. Addition of water to the denser H₂SO₄ can cause localized surface boiling and spattering on the operator.

Trichloroethylene (Cl₂CCHCl) reacts under a variety of conditions with potassium or sodium hydroxide to form dichloroacetylene, which ignites spontaneously in air and explodes readily even at dry-ice temperatures. The compound itself is highly toxic, and suitable precautions should be taken when it is used.

Resources:

National Academy of Sciences (2011), Chapter 4: Physical Hazards, "Prudent Practices in the Laboratory," (pp. 70-73, 145-153)

Kelly, R. and Miller, G. (May 1999), "Storing and Using Peroxidizable Organic Chemicals," Lawrence Livermore National Laboratory, Hazards Control Department, (pp.1-8)