



PROCEDURES FOR THE SAFE STORAGE OF CHEMICALS

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I. Inventory and Inspection

It is the Instructor/Principle Investigators (PI's) responsibility to ensure that chemicals are stored properly in each laboratory and that there is a current written/electronic inventory of all stored chemicals. This inventory should be stored in a central location outside of the laboratory and be immediately accessible to emergency responders 24/7. The inventory should include, but not be limited to, the chemical name and on-hand quantity. Each chemical should be labeled properly and have a designated storage place and should be returned to that place after each use. As a general rule of thumb, it is a good practice to date all chemical containers when first received with the following information to avoid the retention of expired or off-spec chemicals and to ensure the timely disposal of potentially reactive chemicals:

- Date Received
- Date First Opened
- Date to be Discarded

The storage arrangement must be based on hazard class, not the alphabet, and should be posted to show the exact location of the chemical groups. Chemical storage areas should be inspected annually for outdated or unneeded items, illegible labels, leaking containers, etc. Whenever you use chemicals, rotate your stock so that the "oldest" containers are used first. This will help avoid degradation of older chemicals and their containers.

II. Proper Sealing of Chemical Containers

It is very important that containers of highly toxic, highly volatile, malodorous, carcinogenic or reactive chemicals be tightly sealed to prevent leakage, odors, or reaction with air. Make sure that caps and other closures are tight on all hazardous chemicals. An exception is bottles of waste, such as acid-organic mixtures that may generate gas pressure sufficient to burst a tightly sealed bottle. The best seal is the screw-cap with a conical polyethylene or Teflon insert. The caps can then be sealed with tape or Parafilm "M" as a further precaution. Additional protection can include the following: a) Wrapping in an absorbent paper and sealing inside a plastic bag; and, b) Storing the bag inside a metal can with a friction-fitting lid.

III. Smaller Container Sizes - Less is Better

The real, or "life-cycle", cost of a chemical includes its initial purchase price plus the ultimate disposal costs. The quantity of chemicals accumulated in the laboratory should be kept at a minimum to reduce the risk of exposures, fires, and waste disposal problems. In general, limit container size to one (1) gallon in the laboratory. Larger containers should be kept in chemical storage rooms. Smaller chemical container sizes also provide the following advantages:

- Reduced storage hazards
- Reduced storage space
- Safety in handling smaller quantities
- Reduced losses due to out-of-date chemicals
- Minimized cost of disposal of "leftovers"

Frequently, it costs many times more than the original purchase price to dispose of leftover chemicals. The current cost of waste disposal runs from \$10.00 per gallon for non-halogenated solvents to \$75.00 per pound, including the weight of the container, for reactives, e.g., sulfides, cyanides, flammable solids. Waste disposal costs are constantly increasing and the best method for reducing waste disposal costs is to reduce the amount of hazardous waste being generated.

IV. Storage Color Codes

Most chemical manufacturers include chemical storage information on labels. Some chemical manufacturers use color codes on labels and/or caps to indicate health, physical, and chemical hazards. These colors can be used as a guide for storage groups - store same colors together, segregated from other colors. Some manufacturers use the National Fire Protection Association (NFPA 704) hazard warning diamond symbol, the "Hazard Materials Identification System" (HMIS) colored rectangle or bar, and some labels use pictograms, all of which are helpful for storage information. Unfortunately the color schemes are not always consistent among manufacturers. Under most schemes, colors convey the following message:

Red:	Fire Hazard and/or Flammables
White:	Contact Hazard and/or Corrosive (acids or bases)
Blue:	Health Hazard and/or Toxic or Poisonous
Yellow:	Reactivity Hazard and/or Oxidizers
Green, Gray or Orange:	Moderate or slight hazard (general chemical storage)
Striped or "Stop":	Exceptions within the same color code labels (example - yellow labeled chemicals are stored apart from striped yellow labeled chemicals)

V. Chemical Storage Locations

Optimally, incompatible chemicals, such as acids and alkalis, should be stored completely separate from one another to prevent mixing in the event of an accidental spill or release of the materials. Limited storage space within the laboratories, however, prohibits such prudent practice of chemical segregation and storage. If space is limited, it is permissible to store incompatible chemicals in the same storage cabinet provided that the chemicals are segregated according to their hazard class and stored in adequately sized tubs, trays, or buckets while in the cabinet. These secondary containment devices (SCD's) reduce the chance that incompatible chemicals will inadvertently come in contact with each other. Never store chemicals on the floor without adequately sized SCD's. (Adequately sized is defined as sufficient volume to either contain 100% of the volume of the largest stored container or 10% of the total stored volume, whichever is greater.) Never store chemicals in hallways, stairwells, or in any areas generally accessible to the public or subject to temperature extremes.

Laboratory Hoods - Chemicals should not be stored in laboratory hoods because they may impede airflow, reducing the effectiveness of the hood.

Refrigerated Storage - Flammable solvents that require storage at reduced temperature are to be stored only in refrigerators or freezers designed and UL approved for the storage of flammable liquids. "Safety" refrigerators for flammable liquid storage and "explosion-proof" refrigerators are both acceptable. Ordinary domestic refrigerators are not to be used for the storage of flammable liquids because of interior arcing contacts. Because there is no venting of the interior spaces in refrigerators and freezers, all chemicals should have tightly sealed caps. Signs should be applied to the doors of chemical refrigerators stating: NO FOOD, BEVERAGE, OR ICE FOR HUMAN CONSUMPTION."

Cold rooms have closed air-circulation systems and recirculate any leaks and escaped vapors within the chamber. The refrigeration coils in cold rooms are aluminum and subject to damage from corrosive atmospheres. The electrical systems are designed with vapor-proof lights and duplex outlets, but frequently are compromised by extension cords and plug strips. Cold rooms are not acceptable for storage of flammables, dry ice, or liquid chemicals. If these chemicals need to be refrigerated, they are to be stored in an approved refrigerator or freezer, rather than a cold box. A warning sign should be posted on the door as illustrated:

DANGER

NOT EXPLOSION PROOF

NOT VENTILATED

GROUND ALL ELECTRICAL EQUIPMENT

DO NOT STORE DRY ICE

Flammable Liquid Storage – Never store flammable or combustible liquids near potential sources of ignition. Fire Codes limit the storage of flammable liquids to 10 gallons in open storage, 25 gallons in "safety cans", and 60 gallons in "flammable liquid storage cabinets" per laboratory unit. These limits are for the total quantities on hand, including chemicals in storage, chemicals in use, and wastes. See Appendix B for additional information regarding the storage of flammable liquids.

Explosives and Reactives - A reactive chemical is defined as any substance which may, in the presence of air, water, shock, friction, static discharge, or contamination release very large and potentially harmful amounts of energy. See Appendix C for additional information.

If you discover, or suspect you have discovered, any old, potentially explosive or reactive chemicals, **don't handle them.** Contact EHS immediately at either (410) 704-2949 or at safety@towson.edu. Please include the name of the chemical(s), the quantity (1x 1-pint, etc.) and its location (Smith 123, under the hood, etc.)

Peroxide Forming Chemicals - Peroxide formation in solvents and reagents has caused many accidents. Every worker must learn to recognize and safely handle peroxidizable compounds. Peroxides are formed by the reaction of a peroxidizable compound with molecular oxygen through a process called autoxidation or peroxidation. Peroxidizable compounds are insidious. Under normal storage conditions, they can form and accumulate peroxides, which may explode violently when subjected to thermal or mechanical shock. See Appendix D for additional information.

If you discover, or suspect you have discovered, any old peroxide forming chemicals, **don't handle them.** Contact EHS immediately at either (410) 704-2949 or at safety@towson.edu. Please include the name of the chemical(s), the quantity (1x 1-pint, etc.) and its location (Smith 123, under the hood, etc.)

Cabinets and Shelves – If possible, avoid storing chemicals above shoulder height. Large containers (> 1 gallon), liquids, and corrosives should be stored on lower shelves below eye level. Ensure that cabinets and shelves are structurally sound and capable of supporting proposed storage capacities and that they are chemically impervious to any spilled liquids. Do not overcrowd shelves or cabinets.

Cabinets under hoods and laboratory benches may be used for storage of chemicals. However, storage near or under sinks where there may be exposure to water is to be avoided. Under hood storage should be limited to the storage of compatible corrosives. Cabinets for chemical carcinogens or highly toxic chemicals should be locked.

Dessicator Jars or Cabinets - Dessicator jars and cabinets are useful for storage of air and water reactives, toxics, and malodorous chemicals. In case of especially malodorous compounds, i.e., mercaptans, replace the dessicator material with a vapor adsorber (e.g. charcoal) to control odors.

Bench Tops - Storage of chemicals on bench tops is undesirable. Such storage is more vulnerable to accidental breakage by laboratory, housekeeping, and emergency response personnel.

Sinks - The storage of chemicals or chemical containers in or near sinks where there may be exposure to water or unrestricted access to drains is strictly prohibited and constitutes a potentially serious violation of Clean Water regulations.

VI. Storage by Compatibility

Chemicals should be stored in the laboratory according to their chemical compatibility. Chemicals should not be stored in alphabetical order since this practice may place incompatible chemicals next to each other (e.g., sodium cyanide and sulfuric acid) which increases the potential for accidental mixing of incompatible chemicals. The diagram, "Suggested Shelf Storage Pattern," (Appendix A) indicates a recommended arrangement of chemicals according to compatibility. These compatibility groups should be stored separately, especially chemicals with an NFPA 704 or HMIS reactive rating of 3 or higher, and in dedicated labeled cabinets. Within any compatibility group, chemicals may be arranged alphabetically to facilitate ease of retrieval.

The following compatibility groupings are recommended:

Group A - Acids, Inorganics

Store large bottles of acid on low shelves, in special acid cabinets, or cabinets under lab benches. Place acids in plastic trays for secondary containment in case of breakage, especially glass cleaning solutions of chromic acid. Segregate inorganic and oxidizing acids from organic compounds including organic acids and other combustible materials. Segregate nitric acid (>40%) from other inorganic acids. Store acids separate from bases and other reducing agents. Inorganic salts, except those of heavy metals, may be stored in this group. Glacial acetic acid should be stored with flammable and combustible materials since it is combustible.

Group B - Bases

Segregate bases from acids and oxidizers on shelves near the floor. The preferred storage container for inorganic hydroxides is polyethylene instead of glass. Place containers in trays for secondary containment in the event of leakage or breaks.

Group C - Organic Chemicals

Organic compounds should be segregated from inorganics. Organics and inorganics with NFPA 704 or HMIS reactive hazard rating of two (2) or less may be stored together. Chemicals with a reactive hazard rating of three (3) or four (4) are to be stored separately.

Group D - Flammable and Combustible Organic Liquids

Fire Codes limit the quantity of flammable and combustible liquids to 10 gallons in open storage and use, 25 gallons in safety cans, and 60 gallons (30 gallons maximum per cabinet with a maximum of 2 cabinets per room) in flammable storage cabinets. The materials are to be stored away from sources of ignition such as heat, sparks or open flames and are to be segregated from oxidizers.

Group E - Inorganic Oxidizers and Salts

Store inorganic oxidizers in a cool dry place away from combustible materials such as zinc, alkaline metals, formic acid, and other reducing agents. Inorganic salts may also be stored in this group. Store ammonium nitrate separately.

Group F - Organic Peroxides

Certain chemicals are shock or heat sensitive or become that way in storage. Some chemicals form explosive peroxides or react violently with other chemicals. Benzoyl peroxide is shock and heat sensitive. Ethers and other peroxidizable compounds form shock sensitive peroxides in storage. Picric acid is classified as a Class A explosive when it contains less than 10% water. Store shock and heat sensitive chemicals in a dedicated cabinet.

Group G - Reactives

Water Reactives - Water reactives should be stored in cool dry place protected from any water source. A Class D fire extinguisher should be available in case of fire. As an added precaution, containers should be stored in trays or other secondary containers filled with sand.

Pyrophoric (Air Reactives) - Pyrophorics should be stored in a cool, dry place making provision for an air-tight seal. White or yellow phosphorous should be stored under water in glass-stoppered bottles inside a metal can for added protection.

Group H - Cyanides and Sulfides

The compounds react with acids to release highly toxic gases. They must be isolated from acids and other oxidizers.

Group I - Carcinogenic and Highly Toxic Chemicals

A dedicated lockable storage cabinet in a "designated area" is the preferred storage method for highly toxic and carcinogenic chemicals. They should be stored in unbreakable, chemically resistant, secondary containers. The storage cabinet must be posted with a sign stating HIGHLY TOXIC OR CANCER-SUSPECT AGENT. A separate inventory of all highly acute toxics, carcinogens, and reproductive toxins should also be maintained and accessible to emergency responders. See Appendix E for a listing of potential carcinogens.

APPENDIX A

SUGGESTED SHELF STORAGE PATTERN

Compatibility Group	Group Name	Chemical Class
Group A	Inorganic acids, inorganic salts	inorganic acids (except nitric), sulfur, arsenic, halides, sulfates, sulfites, thiosulfates, halogens, phosphorus, phosphates
Group B	Inorganic bases	hydroxides, oxides, silicates, carbonates
Group C	Organics	alcohols, glycols, amines, amides, hydrocarbons, esters, aldehydes, phenol, cresols, organic sulfides, organic acids
Group D	Flammables, combustibles	ethers, aliphatic solvents, aromatic solvents
Group E	Inorganic Oxidizers	borates, chromates, manganates, permanganates, chlorates, perchlorates, chlorites, hypochlorites, hydrogen peroxides, amides, nitrates, nitrites, azides
Group F	Organic peroxides	peroxides, azides, hydroperoxides
Group G	Reactives	air and water reactives, metals and hydrides
Group H	Cyanides, sulfides	cyanides, cyanates, sulfides, carbides, nitrides
Group I	Poisons, carcinogens	severe poisons, carcinogens

APPENDIX B

STORAGE OF FLAMMABLE & COMBUSTIBLE LIQUIDS

Flammable and combustible liquids are separated into the following classes according to the National Fire Protection Association (NFPA):

Class 1A (Highly Flammable)	Flash Point <73°F (22.8°C) Boiling Point <100°F (37.8°C)	Ex: Ethyl ether, Dimethyl sulfide, Petroleum ether
Class 1B Flammable	Flash Point <73° F (22.8° C) Boiling Point ≥100° F (37.8°)	Ex: Acetone, Toluene, Ethanol, Ethyl acetate, Hexane, Gasoline
Class 1C Flammable	Flash Point ≥73° F (22.8° C) Boiling Point <100° F (37.8° C)	Ex: Amyl acetate, Bromopentane, Butyric acid, Hexene, Xylene
Class II Combustible	Flash Point ≥100°F (37.8°C) & <140° (60°C)	Ex: Acetic acid, Cumene, Formaldehyde
Class IIIA Combustible	Flash Point ≥140°F (60°C) & <200°F (93.4°C)	Ex: Benzaldehyde, Ethanolamine, Nitrobenzene

The NFPA has set limits for the storage of flammable liquids. Table 1 below provides the maximum container size for each class of flammable liquid.

Container Type	Flammable Liquid Class			Combustible Liquid Class	
	1A	1B	1C	II	IIIA
Glass	1 Pt	1 Qt	1 Gal	1 Gal	5 Gal
Metal	1 Gal	5 Gal	5 Gal	5 Gal	5 Gal
Safety Can	2 Gal	5 Gal	5 Gal	5 Gal	5 Gal
Metal Drum (DOT)	60 Gal	60 Gal	60 Gal	60 Gal	60 Gal

The following are additional NFPA requirements for storage. For chemical stockrooms, individual evaluations will be necessary and, as a result, may not be bound to these requirements.

1. Not more than 10 gallons of Class I or Class II liquids combined shall be stored outside of a storage cabinet or storage room, except in safety cans.
2. Not more than 25 gallons of Class I or Class II liquids combined shall be stored in safety cans outside of a storage room or storage cabinet.
3. Not more than 60 gallons of Class IIIA liquids shall be stored outside of a storage room or storage cabinet.
4. Any quantity of liquids over this limit must be stored in an inside storage room or storage cabinet.
5. Approved storage cabinets shall not exceed 120 gallons of combustible and flammable liquids and not more than 60 gallons of the total may be flammable liquid. Not more than 3 storage cabinets will be within one fire area of a building.

A fire area, as defined by NFPA, is “an area of a building separated from the remainder of the building by construction having a fire resistance of at least one hour and having all communicating openings properly protected by an assembly having a fire resistance rating of at least one hour.” Each laboratory should be considered an individual fire area.

APPENDIX C

EXPLOSIVE & REACTIVE LABORATORY CHEMICAL HAZARDS

The variety of chemicals commonly present in a research laboratory poses the potential for accidental hazardous chemical reactions or explosions. A hazardous reaction occurs when two or more incompatible chemicals combine to result in an undesirable or uncontrolled reaction with adverse consequences. Such reactions may result when incompatible chemicals are accidentally spilled, when they are inadvertently mixed as chemical waste, or when they are unwittingly combined during experimental procedures. Hazardous reactions may cause any one or more of the following:

- Heat generation
- Fire
- Explosion
- Formation of toxic vapors
- Formation of flammable gases
- Volatilization of toxic or flammable substances
- Formation of substances of greater toxicity
- Formation of shock or friction sensitive compounds
- Pressurization in closed vessels
- Solubilization of toxic substances
- Dispersal of toxic dusts, mists, particles
- Violent polymerization.

It is easy to fall into the trap of becoming complacent with chemicals used everyday in routine procedures. It is prudent to check for incompatibility wherever a change is made in chemical procedures. Incompatibility of chemicals is the prime reason for not storing chemicals on the shelf alphabetically. If there is an accident, the disaster is compounded by the adverse reaction. Material Safety Data Sheets will list "Reactivity Data" in one of the sections on the form. In addition, two good references of incompatible chemical combinations are: Handbook of Reactive Chemical Hazards; L. Bretherick, 6th Edition, 1999 (or most current edition); and Rapid Guide to Chemical Incompatibilities, R. Pohanish and S. Greene, 2nd Edition, 2003 (or most current edition).

Common Reactive Hazards in Laboratories

Listed below are specific chemical reactive hazards in laboratories that can lead to fires or explosions.

Acetylenic Compounds - are explosive in mixtures of 2.5-80% with air at pressures of two or more atmospheres, acetylene (C₂H₂) subjected to an electrical discharge or high temperature decomposes with explosive violence. Dry acetylides detonate on receiving the slightest shock.

Aluminum Chloride (AlCl_3) - should be considered a potentially dangerous material. If moisture is present, there may be sufficient decomposition [to give hydrogen chloride (HCl)] to build up considerable pressure. If a bottle is to be opened after long standing, it should be completely enclosed in a heavy towel.

Ammonia (NH_3) - reacts with iodine to give nitrogen triiodide, which is explosive, and with hypochlorites to give chlorine. Mixtures of NH_3 and organic halides sometimes react violently when heated under pressure.

Dry Benzoyl Peroxide ($\text{C}_6\text{H}_5\text{CO}_2$)₂ - is easily ignited and sensitive to shock. It decomposes spontaneously at temperatures above 50°C . It is reported to be desensitized by addition of 20% water.

Carbon Disulfide (CS_2) - 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 glowing light bulb.

Chlorine (Cl_2) - may react violently with hydrogen (H_2) or with hydrocarbons when exposed to sunlight.

Diazomethane (CH_2N_2) - and related compounds should be treated with extreme caution. They are very toxic, and the pure gases and liquids explode readily. Solutions in ether are safer from this standpoint. (See also "Organic Syntheses," Rabjohn, N., Ed.; Wiley: New York, 1963, Collective Volume IV, pp. 250 - 253).

Diethyl, Isopropyl, and other Ethers - (particularly the branched-chain type) may explode during heating or refluxing because of the presence of peroxides. Ferrous salts or sodium bisulfite can be used to decompose these peroxides, and passage over basic active alumina will remove most of the peroxidic material. Containers are to be marked with the date they are opened and discarded before they are out of date. For more detail, see Safe Handling of Peroxidable Compounds.

Dimethyl Sulfoxide [$(\text{CH}_3)_2\text{SO}$] - decomposes violently on contact with a wide variety of active halogen compounds. Explosions from contact with active metal hydrides have been reported. Its toxicity is still unknown, but it does penetrate and carry dissolved substances through the skin membrane.

Dry Ice - is not to be kept in a container that is not designed to withstand pressure. Containers of other substances stored over dry ice for extended periods generally absorb carbon dioxide (CO_2) unless they have been sealed with care. When such containers are removed from storage and allowed to come rapidly to room temperature, the CO_2 may develop sufficient pressure to burst the container with explosive violence. On removal of such containers from storage, the stopper should be loosened or the container itself should be wrapped in towels and kept behind a shield. Dry ice can produce serious burns (this is also true for all types of cooling baths). Do not store dry ice in walk-in cold rooms because it may result in oxygen-deficient atmosphere.

Drying Agents-Ascarite - is not to be mixed with phosphorus pentoxide (P_2O_5) because the mixture may explode if it is warmed with a trace of water. Because the cobalt salts used as moisture indicators in some drying agents may be extracted by some organic solvents, the use of these drying agents should be restricted to gases.

Ethylene Oxide (C_2H_4O) - has been known to explode when heated in a closed vessel. Experiments using ethylene oxide under pressure should be carried out behind suitable barricades.

Halogenated Compounds - Chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), and other halogenated solvents should not be dried with sodium, potassium, or other active metal; violent explosions are usually the result of such attempts. Many halogenated compounds are toxic.

Hydrogen peroxide (H_2O_2) - stronger than 3% can be dangerous; in contact with the skin, it may cause severe burns. Thirty percent H_2O_2 may decompose violently if contaminated with iron, copper, chromium, other metals or their salts.

Liquid-Nitrogen Cooled Traps - when open to the atmosphere rapidly condense liquid air. When the coolant is removed, a pressure buildup may occur sufficient to shatter glass equipment. Only sealed or evacuated equipment should be cooled with liquid nitrogen.

Lithium Aluminum Hydride ($LiAlH_4$) - should not be used to dry methyl ethers or tetrahydrofuran; fires from this are very common. The products of its reaction with CO_2 have been reported to be explosive. Carbon dioxide or bicarbonate extinguishers are not to be used against $LiAlH_4$ fires, which should be smothered with sand or a metal-X extinguisher.

Oxygen Tanks - serious explosions have resulted from contact between oil and high-pressure oxygen. Oil should not be used on connections to an O_2 cylinder or regulator.

Ozone (O_3) - is a highly reactive and 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.

Palladium or Platinum on Carbon, Platinum Oxide, Raney Nickel, and other Catalysts - should be filtered from catalytic hydrogenation reaction mixtures carefully. The recovered catalyst is usually saturated with hydrogen and highly reactive and, thus, will ignite spontaneously on exposure to air. Particularly in large-scale reactions, the filter cake should not be allowed to become dry. The funnel containing the still-moist catalyst filter cake should be put into a water bath immediately after completion of the filtration.

Another hazard in working with such catalysts is the danger of explosion if additional catalyst is added to a flask in which hydrogen is present.

Parr Bombs - used for hydrogenations have been known to explode. They should be handled with care behind shields, and the operator should wear goggles.

Perchlorates - the use of perchlorates should be avoided wherever possible. Perchlorates should not be used as drying agents if there is a possibility of contact with organic compounds or in proximity to a dehydrating acid strong enough to concentrate the perchloric acid (HClO_4) to more than 70% strength (e.g., in a drying train that has a bubble counter containing sulfuric acid). Safer drying agents are to be used.

Seventy percent (70%) HClO_4 can be boiled safely at approximately 200°C , but contact of the boiling undiluted acid or the hot vapor with organic matter, or even easily oxidized inorganic matter (such as compounds of trivalent antimony), will lead to serious explosions. Oxidizable substances must never be allowed to contact HClO_4 . Beaker tongs, rather than rubber gloves should be used when handling fuming HClO_4 . Perchloric acid evaporations should be carried out in a hood that has a good draft. Frequent (weekly) washing out of the hood and ventilator ducts with water is necessary to avoid danger of spontaneous combustion or explosion if this acid is in common use.

Permanganates - are explosive when treated with sulfuric acid. When both compounds are used in an absorption train, an empty trap is to be placed between them.

Peroxides (inorganic) - when mixed with combustible materials, barium, sodium and potassium peroxides form explosives that ignite easily.

Phosphorus (P) - (red and white) forms explosive mixtures with oxidizing agents. White (also called yellow) P should be stored under water, in glass, because it is spontaneously flammable in air. The reaction of P with aqueous hydroxides gives phosphine, which may ignite spontaneously in air or explode.

Phosphorus Trichloride (PCl_3) - reacts with water to form phosphorous acid, which decomposes on heating to form phosphine, which may ignite spontaneously or explode. Care should be taken in opening containers to PCl_3 , and samples that have been exposed to moisture should not be heated without adequate shielding to protect the operator.

Potassium (K) - is in general 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 kerosene (see Sodium). Potassium may also form peroxides even while stored under oil.

Residues from Vacuum Distillations - (for example, ethyl palmitate) have been known to explode when the still was vented to the air before the residue was cool. Such explosions can be avoided by venting the still pot with nitrogen, by cooling it before venting, or by restoring the pressure slowly.

Sodium (Na) - should be stored in a closed container under kerosene, toluene or mineral oil. Scraps of Na or K are to be destroyed by reaction with n-butyl alcohol. Contact with water is to be avoided because Na reacts violently with water to form H_2 with evolution of sufficient heat to cause ignition. Use sand or metal-X extinguisher on alkali metal fires. Do not use CO_2 .

Sulfuric Acid (H_2SO_4) - 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 dessicator is moved. The use of H_2SO_4 in melting point baths should be avoided. (Silicone oil should be used). To dilute H_2SO_4 , add the acid slowly to cold water.

Trichloroethylene (Cl_2CCHCl) - reacts under a variety of conditions with potassium or sodium hydroxide to form dichloroacetylene, which ignites spontaneously in air and detonates readily even at dry-ice temperatures. The compound itself is highly toxic and suitable precautions should be taken when it is used as a degreasing solvent. Methyl chloroform (1,1,1-trichloroethane) is a less toxic substitute.

APPENDIX D

SAFE HANDLING OF PEROXIDIZABLE COMPOUNDS

Peroxide formation in solvents and reagents has caused many accidents. Every worker must learn to recognize and safely handle peroxidizable compounds. Peroxides are formed by the reaction of a peroxidizable compound with molecular oxygen through a process called autoxidation or peroxidation. Peroxidizable compounds are insidious. Under normal storage conditions, they can form and accumulate peroxides, which may explode violently when subjected to thermal or mechanical shock.

Peroxides in solution at concentrations up to about 1 percent do not normally present thermal or shock hazards. Such solutions may be safely disposed of or treated to remove peroxides. However, should crystals form in a peroxidizable liquid or should discoloration occur in a peroxidizable solid, peroxidation may have already occurred. The product would then be considered extremely dangerous and should be disposed of without opening the container.

To prevent accidents caused by peroxidizable compounds, laboratory safety procedures should emphasize:

- Recognition of chemical structures that may form peroxides (See Table I, Tab A)
- Use of warning labels
- Controlled inventory of peroxidizable compounds
- Use of peroxide detection tests and peroxide removal procedures
- Proper safety equipment and process procedures

I. Peroxidizable Compounds

Some of the specific compounds that form peroxides during storage are included in Lists A, B and C in Table II, Tab A. Those that form peroxides that may explode even without being concentrated are in List A. List B includes chemical that are dangerous when concentrated by distillation or evaporation. Vinyl monomers that can form peroxides that may initiate explosive polymerization of the monomers are found in List C.

Peroxide accumulation is a balance between the rate of peroxide formation and the rate of peroxide degradation for the particular substance under the environment of the sample. For example, certain highly reactive compounds, such as organometallics, accumulate peroxide at low temperatures because the peroxide degradation rate is slowed relative to the formation rate. In contrast, less reactive compounds, such as hydrocarbons or ethers, are usually best kept at low temperatures.

The more volatile the peroxidizable compound, the easier it is to concentrate the peroxides. One should also remember that pure compounds are more subject to peroxide accumulation because impurities may inhibit peroxide formation or catalyze their slow decomposition.

II. Detection of Peroxides

Testing of ethers and other peroxide-forming solvents prior to distillation should be routine.

Peroxide Test Strips - Commercial test strips are available from Aldrich Chemical Company. These strips are convenient to use; however, they do not have the universality or the sensitivity of the ferrous thiocyanate test and their shelf-life is limited.

Ferrous Thiocyanate Test - Mix a fresh solution in the following proportions:

- 5 mL of 1% ferrous ammonium sulfate
- 0.5 mL of 0.5M sulfuric acid
- 0.5 mL of 0.1M ammonium thiocyanate
- Decolorize with a trace of zinc dust if necessary

Shake an equal quantity of the solvent to be tested with the above reagent. The relation between color change and peroxide content is shown in Table III, Appendix D.

III. Storage

Quantities of peroxidizable compounds should be purchased according to short-term needs. Only purchase quantities needed for immediate use. Never stockpile. For instance, buy six (6) one pound cans of ether instead of one six pound can. Purchase of package sizes corresponding to use requirements to minimize exposure to air from multiple openings of the container. A tight cap on a nearly full bottle probably provides almost total protection against peroxide formation.

Peroxide accumulation can be held to very low levels by storage in reasonably full containers (25% maximum headspace) with TIGHT caps that are replaced promptly after use. Still more protection can be provided by flushing the headspace over peroxidizable compounds with nitrogen (inert gas) before closing the container. Vinyl monomers (List C, Table II, Tab A) containing certain inhibitors are exceptions and require air in the headspace.

The use of oxidation inhibitors is especially important in the safe handling of peroxidizable materials. Hydroquinone, alkyl phenols, aromatic amines, or similar materials are recommended by the manufacturers as being effective in preventing peroxide formation during storage of peroxidizable compounds. The inhibitor selected should be compatible with use or purity requirements of the compounds. A program of periodic testing and replenishing inhibitor levels should be followed during storage of peroxidizable materials.

Each laboratory should maintain a current on-hand inventory of peroxidizable compounds. This listing should be reviewed every semester and stored in a central location outside of the laboratory and immediately accessible to emergency responders. Those that are out of date should be immediately discarded through EHS.

List A (Table II, Tab A) materials should be evaluated for peroxide content at least every three (3) months after opening and re-dated if safe, treated or discarded. Before disposal of any List A material, review the properties of the material to ensure safe disposal.

List B (Table II, Tab A) materials should not be stored longer than twelve (12) months after opening unless a suitable test shows they have not accumulated peroxide. If List B material give a significantly positive test (red by the ferrous thiocyanate test), but must be retained, it must be treated to remove peroxide, repackaged, shown by test to be free of peroxide, and then re-dated on its label.

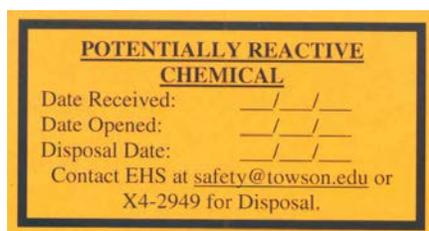
List C (Table II, Tab A) materials are vinyl monomers and should be stored for no longer than twelve (12) months unless test results show them to be free of peroxide. Commercial vinyl monomers usually contain additives (inhibitors), which inhibit peroxidation. Generally, storage of inhibited vinyl monomers should be under air rather than nitrogen or other inert atmosphere, because customary inhibitors are phenolic compounds, which require oxygen for their action. Most vinyl monomers may be polymerized without removal of inhibitor by proper adjustment of initiator concentration, thus making the isolation of the more hazardous uninhibited material unnecessary.

Uninhibited List C materials can be a significant hazard. Quantities of such uninhibited monomers greater than 500 g should be stored no longer than 24 hours. Small samples (less than 10 g may be stored longer than 24 hours with discretion. Generally storage of uninhibited vinyl monomers should be under nitrogen and below room temperatures. For storage in excess of 24 hours, a suitable inhibitor should be added, and its name and quantity should be placed on the label.

In addition, each container of peroxide-forming chemicals must have the following dates written on the label.

- Date Received
- Date First Opened
- Date to be Discarded

In some cases, where peroxides are chemically removed, a notation on the label would indicate the new date. EHS has pre-printed labels available. Contact EHS at (410) 704-2949 to request them.



**POTENTIALLY REACTIVE
CHEMICAL**
Date Received: ___/___/___
Date Opened: ___/___/___
Disposal Date: ___/___/___
Contact EHS at safety@towson.edu or
X4-2949 for Disposal.

Peroxide-forming chemicals should be stored together in full, air-tight opaque containers at temperatures below 30C and in the dark. Use only refrigerators designated and UL approved for flammable liquids or one that is explosion-proof as arcing contacts have been removed that might otherwise ignite vapors.

IV. Removal of Peroxides

Peroxide impurities in water-insoluble solvents (ether, hydrocarbons) are easily purified by shaking with the following solution:

- 60 g of ferrous sulfate
- 6 mL of concentrated sulfuric acid
- 110 mL of distilled water

Water is introduced by this method so post-drying will be required if a dry solvent is needed.

V. Disposal

Immediately set aside and **DO NOT USE** any peroxide-forming chemicals that have formed crystals, precipitate, solids or an oily viscous layer, or any rusted, damaged, undated or suspicious containers of peroxide-forming chemicals.

If you discover, or suspect you have discovered, any old, potentially explosive or reactive chemical, **don't handle them.** Contact EHS immediately at either (410) 704-2949 or at safety@towson.edu. Please include the name of the chemical(s), the quantity (1x 1-pint, etc.) and its location (Smith 123, under the hood, etc.).

Never attempt to force open a rusted or jammed cap or a cap encrusted with scale on a container of peroxide-forming chemicals. Never attempt to clean by scraping or rubbing glassware or other containers if an oily deposit or crusty residue is present.

Empty containers of ethers and other peroxide-formers are to be flushed with water before discarding. Empty containers are not regulated for disposal as hazardous wastes and may be disposed via traditional domestic waste channels.

VI. Distillation and Evaporation Precautions

Testing peroxidizable solvents for peroxides prior to distillation or evaporation should be routine. One common error is distilling too close to dryness; leave at least 10% bottom to ensure complete safety.

VII. Safety Audit

A safety audit should be performed before starting any chemical experiment in the laboratory. This would include a review of possible hazards from the use of peroxidizable chemicals in the experiment. Peroxidation may have already occurred in one or more of the starting materials; it may occur during the process, or in the storage of the products. In every chemical process, the following factors should be considered relative to (a) the starting materials, (b) the process itself, and (c) the products:

- Structure - are peroxidizable structures present or being formed?
- Process conditions - will the process condition favor initiation of peroxidation and accumulation of peroxides?
- Storage - will storage containers and conditioners reduce peroxide initiation and accumulation, and are all products properly inhibited and labeled?

If the audit indicates that peroxidation or peroxides are present, the described procedures of handling, testing, and removal should be followed.

As noted previously, peroxidation in a chemical process may not only be a serious hazard because of the explosion potential, but it also may affect the results of an experiment because of lower yield and unwanted impurities

TAB A
APPENDIX D

TABLE I
PEROXIDE-FORMING STRUCTURES

Organic structures (In approximate order of decreasing hazard)

1. Ethers with alpha hydrogen atoms (isopropyl ether, ethyl ether, glyme)
2. Acetals with alpha hydrogen atoms (acetal, benzylacetal)
3. Olefins with allylic hydrogen atoms (butylene, cyclohexene)
4. Chloroolefins and fluoroolefin (tetrafluoroethylene)
5. Vinyl halides, esters, and ethers (vinylidene chloride, vinyl chloride, vinyl acetate)
6. Dienes (butadiene, chloroprene)
7. Vinylacetylenes with alpha hydrogen atoms (diacetylene, vinylacetylene)
8. Alkylacetylenes with alpha hydrogen atoms (3-methyl-1-butyne)
9. Alkylarenes that contain tertiary hydrogen atoms (isopropyl benzene)
10. Alkanes and cycloalkanes that contain tertiary hydrogen atoms (ethylcyclohexane)
11. Acrylates and methacrylates (methylmethacrylate, acrylonitrile)
12. Secondary alcohols (secbutyl alcohol, diphenylmethanol)
13. Aldehydes (benzaldehyde)
14. Ketones with alpha hydrogen atoms (diisopropyl ketone, MEK)
15. Ureas, Uramides, lactams with hydrogen atom on carbon atom attached to nitrogen (N-ethylacetamide, N-isopropylacetamide)

TABLE II

Common Compounds That Form Peroxides During Storage

<u>List A – Red Label</u> (Three months) Peroxide Hazard on Storage	<u>List B – Yellow Label</u> (Twelve months) Peroxide Hazard on Concentration	<u>List C – Yellow Label</u> (Twelve months) Hazard Due to Peroxide Initiation of Polymerization
Isopropyl ether	Ethyl ether	Butadiene
Divinyl acetylene	Tetrahydrofuran	Tetrafluoroethylene
Vinylidene chloride	Dioxane	Chlorotrifluoroethylene
Potassium metal	Acetal	Styrene
Sodium amide	Methyl i-butyl keton	Vinyl acetylene
	Ethylene glycol dimethyl ether	Vinyl acetate
	(glyme)	Vinyl chloride
	Vinyl ethers	Vinyl pyridine
	Dicyclopentadiene	Chlorobutadiene (chloroprene)
	Diacetylene	9, 10 Dihydroanthracene
	Methyl acetylene	Idene
	Cumene	Dibenzocyclopentadiene
	Tetrahydronaphthalene	
	Cyclohexene	
	Methylcyclopentane	
	t-Butyl alcohol	

* When stored as a liquid, the peroxide-forming potential increases and certain of these monomers (especially butadiene, chloroprene, and tetrafluoroethylene) should then be considered as List A compounds.

TABLE III

THE FERROUS THIOCYANATE TEST

Relation between Color Change and Peroxide Content of a Compound

Color	Per Cent of Peroxide as H₂O₂
Barely discernible pink	0.001
Pink to cherry red	0.002
Red	0.008*
Deep red	0.04*

*A percentage of 0.008 or more is a hazard

APPENDIX E

POTENTIAL CARCINOGENS

For storage purposes, the following is a list of substances NIOSH considers to be potential occupational carcinogens.

A number of the carcinogen classifications deal with groups of substances: aniline and homologs, chromates, dinitrotoluenes, arsenic and inorganic arsenic compounds, beryllium and beryllium compounds, cadmium compounds, nickel compounds, and crystalline forms of silica. There are also substances of variable or unclear chemical makeup that are considered carcinogens, coal tar pitch volatiles, coke oven emissions, diesel exhaust and environmental tobacco smoke.

Some of the potential carcinogens listed in this index may be re-evaluated by NIOSH as new data become available and the NIOSH recommendations on these carcinogens either as to their status as a potential occupational carcinogen or as to the appropriate recommended exposure limit may change.

A

Acetaldehyde
2-Acetylaminofluorene
Acrylamide
Acrylonitrile
Aldrin
4-Aminodiphenyl
Amitrole
Aniline and homologs
o-Anisidine
p-Anisidine
Arsenic and inorganic arsenic compounds
Arsine
Asbestos
Asphalt fumes

B

Benzene
Benzidine
Benzidine-based dyes
Beryllium
Butadiene
tert-Butyl chromate; class, chromium hexavalent

C

Cadmium dust and fume
Captafol
Captan
Carbon black (exceeding 0.1% PAHs)
Carbon tetrachloride
Chlordane
Chlorinated camphene
Chlorodiphenyl (42% chlorine); class polychlorinated biphenyls
Chlorodiphenyl (54% chlorine); class polychlorinated biphenyls
Chloroform
Chloromethyl methyl ether
bis(Chloromethyl) ether
B-Chloroprene
Chromium, hexavalent [Cr(VI)]
Chromyl chloride; class, chromium hexavalent
Chrysene
Coal tar pitch volatiles; class, coal tar products
Coke oven emissions

D

DDT (dichlorodiphenyltrichloroethane)
Di-2-ethylhexyl phthalate (DEHP)
2,4-Diaminoanisole
o-Dianisidine-based dyes
1,2-Dibromo-3-chloropropane (DBCP)
Dichloroacetylene
p-Dichlorobenzene
3,3'-Dichlorobenzidine
Dichloroethyl ether
1,3-Dichloropropene
Dieldrin
Diesel exhaust
Diglycidyl ether (DGE); class, glycidyl ethers
4-Dimethylaminoazobenzene
Dimethyl carbomoyl chloride
1,1-Dimethylhydrazine; class, hydrazines
Dimethyl sulfate
Dinitrotoluene
Dioxane

E-G

Environmental tobacco smoke
Epichlorohydrin
Ethyl acrylate
Ethylene dibromide
Ethylene dichloride
Ethylene oxide
Ethyleneimine
Ethylene thiourea
Formaldehyde
Gallium arsenide
Gasoline

H-K

Heptachlor
Hexachlorobutadiene
Hexachloroethane
Hexamethyl phosphoric triamide (HMPA)
Hydrazine
Kepone

M

Malonaldehyde
Methoxychlor
Methyl bromide; class, monohalomethanes
Methyl chloride
Methylhydrazine
Methyl iodide; class, monohalomethanes
Methyl hydrazine; class, hydrazines
4,4'-Methylenebis(2-chloroaniline) (MBOCA)
Methylene chloride
4,4-Methylenedianiline (MDA)

N

a-Naphylamine
B-Naphylamine
Nickel, metal, soluble, insoluble, and inorganic; class, nickel, inorganic
Nickel carbonyl
Nickel sulfide roasting
4-Nitrobiphenyl
p-Nitrochlorobenzene
2-Nitronaphthalene
2-Nitropropane
N-Nitrosodimethylamine

P

Pentachloroethane; class, chloroethanes
N-Phenyl-*b*-naphthylamine; class, *b*-naphthalene
Phenyl glycidyl ether; class, glycidyl ethers
Phenylhydrazine; class, hydrazines
Propane Sultone
B-Propiolactone
Propylene dichloride
Propylene imine
Propylene oxide

R-S

Radon
Rosin core solder, pyrolysis products (containing formaldehyde)
Silica, crystalline cristobalite/quartz/tripoli and tridymite
silica, fused
Soapstone, total dust silicates

T

Tremolite silicates
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD) (dioxin)
1,1,2,2-Tetrachloroethane
Tetrachloroethylene
Titanium dioxide
o-Tolidine-based dyes
o-Tolidine
Toluene diisocyanate (TDI)
Toluene diamine (TDA)
o-Toluidine
p-Toluidine
1,1,2-Trichloroethane; class, chloroethanes
Trichloroethylene
1,2,3-Trichloropropane

U-Z

Uranium, insoluble compounds Uranium, soluble compounds
Vinyl bromide; class, vinyl halides
Vinyl chloride
Vinyl cyclohexene dioxide
Vinylidene chloride (1,1-dichloroethylene); class, vinyl halides
Welding fumes, total particulates
Wood dust
Zinc chromate; class, chromium hexavalent