Appendix F: Preventing Chemical Incompatibility Hazards

It is important that you know how to avoid chemical incompatibility hazards. When incompatible chemicals mix, a violent reaction, explosion, or fire can result. These incidents can result in injuries, fatalities, environmental, and property damage. Some chemical mixtures generate a toxic gas. When using and storing chemicals, a chemical's compatibility with its container and closure is important to prevent leaks, releases, and container failure. In a fire or other disaster, stored containers break and adjacent chemicals can combine which can promote a fire or exacerbate an emergency. To address chemical storage and compatibility safety, consider what would happen in an emergency. What threat would your bottles of oxidizers and flammable liquids pose if fire hoses were dragged through the aisles of your laboratory?

Preventing chemical incompatibility hazards in a laboratory is best addressed from four perspectives:

- **Containment of chemicals**. Proper containers and closures can prevent leaks.
- **Storage of laboratory chemicals**. Store flammable liquids in fire safe cabinets.
- **Spatial considerations during storage**. For example, keep concentrated acids away from cyanide salts.
- **Mixing chemicals**. Learn how to prevent mixing hazards. For instance, incompatible chemical wastes must not be placed in the same container.

> Consider chemical compatibility when storing chemicals, packaging chemicals for transport, and pouring a variety of solvents into carboys.

Because the scope and complexity of this topic, this Appendix is not meant to be comprehensive. For more information consult, the Safety Data Sheet's (SDS's) for the chemicals, chemical incompatibilities reference manuals, or Environmental Health and Safety.

There are far more combinations of chemical mixtures that are compatible, as opposed to incompatible, so it is easier to discuss and explain what not to do when combining or storing chemicals.

CONTAINMENT TO PREVENT INCOMPATIBILITY HAZARDS

There are four key concepts to remember when considering use and containment incompatibilities:

1) use of appropriate containers,
2) secondary containment for liquids and high hazard chemicals,
3) use of designated cabinets and areas for high hazard chemicals, and
4) other use and containment incompatibilities.

Use Appropriate Containers

Proper containers for chemical storage will not only help prevent expanding the severity of an event, but will also help to protect the laboratory worker during normal use and storage.

- Use the appropriate storage containers. Store chemicals in their original containers; transfer chemicals only to containers made of like materials.
- Containers must be compatible with their contents. For instance, do not store hydrofluoric acid in a glass container.
- Buy smaller quantities. Part F of this Guide describes waste minimization. As some containers age, their caps and main vessel can become brittle. In addition, smaller bottles are less prone to shatter when accidentally dropped.
- Use safety cans for storage of flammable liquids. Safety cans are acceptable for storing larger volumes of flammable liquids. Fire codes allow only 10 gallons of flammable liquids in a lab if stored in conventional containers of glass, metal, or plastic. However, if stored in a UL-approved flammable liquid storage cabinet, up to 60 gallons may be stored in a single cabinet with no more than three cabinets in a fire area.

Do not store hydrofluoric acid in a glass container.

Choose Safer Containers to Reduce Breakage

When possible, buy extremely hazardous or reactive chemicals in plastic coated bottles. These are coated with a thin layer of polymer to help absorb shock, prevent breakage, and act as a secondary container in the event the bottle is broken. The safest container is a UL approved safety can. The least safe is an uncoated glass container that will shatter if dropped on the floor.

Use Appropriate Closures, Caps, and Seals

Chemicals should not react with or attack the container or the cap. Some chemicals require special devices such as vent caps for alleviating unpreventable pressure buildup. Other chemicals, such as dibenzoyl peroxide, a potential explosive material, require the container be non-rigid to prevent shock transfer, non-conductive to static electricity buildup, and have no screw cap to prevent friction from removing a threaded cap.

Use Secondary Containment

For liquid and high hazard chemicals, secondary containers are an effective tool to prevent reactions between incompatible chemicals. It is best to use secondary containers made of materials that are non-reactive, such as polyethylene. When storing reactive materials, secondary containment can prevent degradation and reactions that occur during storage, as well as prevent interaction of materials. For transporting bottles in hallways or from the stockroom, use a specially designed carrier or a five-gallon plastic bucket to prevent spills. See the Chemical Storage and Management section of Part D for more information.

Secondary containment means using a second outer container to collect and contain spills or leaks from a primary chemical container. Secondary containment can be a plastic tray, a bottle carrier or a wide-mouthed jar containing a smaller bottle.

Designated Cabinets and Areas for High Hazard Chemicals

Specific storage requirements have been identified for acids, flammable liquids, liquids in general, and gas cylinders.

Flammable Liquids

Large volumes of flammable liquids, more than ten gallons per fire area (laboratory), must be stored in an approved flammable liquid cabinet or safety can. All containers of flammable liquids are to be stored in these cabinets. Refer to Part D of this Guide for more information on flammable liquid storage cabinets.

Acid (Corrosive) Cabinets

Bottles of acid should be stored in an acid (corrosive) cabinet. While acids and bases are both considered corrosive, care must be taken to not store acids and bases in the same cabinet. It is particularly important to avoid storing ammonium hydroxide and strong mineral acids in the same cabinet.

Oxidizing acids, such as fuming nitric, fuming sulfuric and nitric should be stored separately, in a secondary container within an acid cabinet. Polypropylene boxes for use in acid cabinets are available commercially.

> Glacial acetic acid is an unusual case due to its flammability. Keep glacial acetic acid in a fire safe cabinet to protect it in a fire, but place the bottle within secondary containment to separate it from other flammable liquids.

Further Compatibility Considerations for Chemical Storage

Incompatibility of stored chemicals is a serious concern in the event of an accident, container breakage, a spill, a tornado, or a fire. In a laboratory fire, shelves collapse, lighting fixtures fall, and firefighters may need to drag hoses through your laboratory that may be smoke filled. To prepare for such emergencies, make sure you store your chemical containers in ways that do not add to the hazardous situation. One of the best ways to avoid complication due to incompatible storage is through proper storage of laboratory chemicals. Proper storage includes meeting special storage requirements, containment, and storage compatibilities for open stock chemicals.

In a disaster, some of the containers of chemicals can break and the contents will mix and react with each other. So, when you store chemicals, try to keep incompatible chemicals away from each other.

Storage of Liquids

When storing liquids, store them as close to the floor (but not on it) as possible. This will eliminate the possibility of tipping a bottle over and having a stream of chemicals flowing from above your line of vision. If a bottle stored near the floor tips, it is also possible that it will not break. By storing solids above liquids, the threat of incompatible chemicals mixing in the event of a broken bottle is also lessened.

Spatial Considerations for Open Stock

Keep stored incompatible chemicals apart from one another. Keep dissimilar materials apart by distance, by shelf, by shelving unit, drawer, or by cabinet.

By storing flammable liquids in a flammables cabinet, acids in an acid cabinet, keeping liquids stored below eye level and following the containment ideas listed above, you will eliminate many of the compatibility problems associated with chemical storage.

> Most laboratories should have a flammables cabinet, an acid cabinet, and liquids on lower shelves within trays.

PREVENTING BINARY MIXTURE INCOMPATIBILITY HAZARDS

Accident case histories are full of unfortunate chemical combinations whether intentional or inadvertent. Of course, in planning a chemical reaction one wants the chemicals to react. Obtaining a successful, safe reaction will depend upon proper dilution, heating or cooling, mixing order, and mixing efficiency. There are unforeseen reactions that may occur, such as, but not limited to: a) a solvent to dissolve a solid, b) a combination of solvents for a chromatographic procedure, c) chemical mixtures that are used for effective cleaning of equipment. Even among chemicals that are considered organic solvents, there are combinations that can react vigorously enough to melt a plastic waste collection container (carboy).

> Binary mixture compatibility applies to preventing violent reactions in your lab work, in packaging chemicals for transport, and when pouring a variety of solvents into waste solvent collection carboys.

Safe Procedures for Chemical Work

One of the best ways to minimize the chance of chemical mixture hazards is to have good chemical safety procedures in place. These include:

- Having a written Chemical Hygiene Plan that takes into account the specific hazards of your laboratory (See Appendix B and Appendix C).
- Laboratory supervisors routinely observing hazardous processes, and periodically reviewing and updating procedures.
- Laboratory supervisors providing the correct protective equipment and making sure it is used correctly (See Part D).
- Having Safety Date Sheets (SDS's) available for the chemicals that are used in your laboratory and consulting them for incompatibilities.

Safe Mixing of Chemicals

Use sensible precautions when conducting an exothermic (heat releasing) reaction. Add the reactants slowly, and keep the reaction vessel cool (Use a water bath, add ice). When making an acid solution, starting with a concentrated acid, always add the acid to the water (never add water to the concentrated acid).

Collection of Chemical Wastes

Do not mix waste unless specifically approved in Part G and Appendix A of this Guide. In general, it is acceptable to combine common high volume use waste organic solvents. For instance, it is fine to mix ethanol, acetone, hexane, and ethyl acetate. Part G instructs you how to keep waste solvents separate.

Binary Mixture Incompatibilities

Accidental mixing of one chemical with another may result in a vigorous and hazardous chemical reaction. Generation of toxic gases, heat, possible overflow or rupturing of containers, fire, and even explosions are possible consequences of such reactions. These reactions may be immediate or they might take some time or outside help to gain momentum.

Realize though, that these violent reactions will occur only if the chemicals are mixed together, not when the incompatible materials are merely present in the same room at the same time. Chemical compatibility must be taken into account when planning for storage of chemicals, when packaging chemicals for transport, and especially when pouring a variety of solvents into carboys.

An improperly packaged box of chemicals could easily turn into a bomb, bonfire, or toxic gas bomb if the box falls on the ground and the bottles break, resulting in the mixture of incompatible chemicals.

The Chemical Compatibility Charts on the following pages are derived in part from Leslie Bretherick's *Handbook of Reactive Chemical Hazards*. The charts show chemical combinations believed to be dangerously reactive in the case of accidental mixing. The chart provides a broad grouping of chemicals with an extensive variety of possible binary combinations.

The kinds of things to be concerned with are toxic or explosive generation of gas, fire from oxidizers meeting combustibles, explosive liquids formed in accidental mixing, or a heat of reaction causing boiling and or splattering of hazardous substances.

As with any incompatibility chart there may be some combinations between the groups that would not react.

STRONG OXIDIZER-REDUCER INCOMPATIBILITIES

Strong oxidizers should never be allowed to come in contact with or mix with or be packaged with any reducer. Take all appropriate precautions to avoid the accidental mixing and reaction of oxidizers and reducers. By separating oxidizers from fuels, such as flammable liquids, you eliminate one of the major concerns with incompatible storage. By segregating oxidizers and reducers, you will further reduce the problems involved with storage of oxidizing chemicals.

Oxidizers	Reducers
Benzoyl peroxide Bromine Chlorimides Hydrogen peroxide solutions Metal peroxides (e.g. sodium, barium, zinc) NBS (N-bromosuccinimide) NCS (N-chlorosuccinimide) Osmium tetroxide **Salts and solutions of:** Bromates, Bromites, Chlorates, Chlorites, Chromates, Dichromates, Hypochlorites, Iodates, Manganates, Nitrates, Nitrites, Percarbonates, Perchlorates, Periodates, Permanganates, Persulfates, Selenates, Vanadates	**Group I metals**: Cesium, Potassium, Lithium, Sodium, Rubidium, and some salts of these metals **Group II metals**: Beryllium, Magnesium, and Calcium powder, and some salts of these metals, including Grignard reagents, Barium and Strontium **Transition metals**: Cobalt, Chromium, Iron, Manganese, Nickel, and Vanadium carbonyls, Aluminum, Iron, Nickel, and Zinc powders **Catalysts**: Palladium, Platinum, Rhodium, and Ruthenium **Others**: Alkenes, Alkynes, Amines, Anilines, Carbon powder, Hydrazine, Hydroxylamine, Mercaptans, Indoles, Phenols, Pyrroles, Phosphines, Phosphorus (any color), Phosphorus hydrides, Sulfides, Silicone hydrides, Sodium dithioninte or hydrosulfite **Solid salts and solutions of:** Hypophosphites, Phosphites, Sulfites, Sulfides, Thiocyanates, Thiosulfates, Cyanides, Sulfur powder.

Reactives

One of the primary concerns with storage incompatibilities of reactive materials is that they decompose during storage. Details of peroxide-forming chemicals can be found in **Part B** of this Guide. Several chemicals that are considered reactive upon storage are listed below with their cause for reaction.

Incompatibility with Water or Moist Air

Some common laboratory chemicals have a great affinity for or react vigorously with water. Take care not to store or use these chemicals in damp areas.

Immediate Violent Reaction with Water

Aluminum Chloride, anhydrous
Boron tribromide
Chlorosulfonic acid
Diketene
Fuming sulfuric acid (Oleum)
Magnesium Chloride, anhydrous
Methyl fluorosulfonate
Oxalyl chloride
Phosphorus pentachloride
Phosphorus pentoxide
Silicon tetrachloride
Triethyl oxonium hexafluorophosphate
Trifluoroacetic anhydride
Trifluoromethane sulfonic anhydride
Trimethyl oxonium hexafluorophosphate

Reaction with Water That Slowly Accelerates to Violence

Acetyl chloride
Alkyl isocyanates
Chloroformate esters
Methane sulfonyl chloride
Phosphorus oxychloride
Phosphorus tribromide
Phosphorus trichloride
Sulfur mono-, di-, and tetra-chlorides
Sulfur trioxide
Sulfuryl chloride
Thionyl chloride
Thiophosphoryl chloride

Produces Chlorine: A) Spontaneously B) Due to Water Absorption C) Due to Carbon Dioxide Absorption

Calcium hypochlorite (B, C)
Phosphorus pentachloride (A)
Sodium hypochlorite solution (C)
Sulfuryl chloride (A)

Immediate Violent Reaction with Water and Ignition in Air As a Result of Reaction

Calcium carbide
Group 1A, 2A, 3A alkyls, amides, hydrides and nitrides
Lithium aluminum hydride (Lithium tetrahidridoaluminate)
NaK (sodium-potassium alloy)
Potassium metal
Sodium metal

Absorption of Atmospheric Water Causes Heat and/or Pressure Build-Up

Alkyl chloroformates
Calcium chloride, anhydrous
Calcium oxide, anhydrous (unslaked lime)

Absorption of Atmospheric Water Causes Slow Hydrogen Chloride Release

Arsenic, antimony, and bismuth trichloride
Silicon, titanium, vanadium, germanium and tin tetrachloride, anhydrous
Toluenesulfonyl chloride
Dichlorodimethyl silane

Absorption of Atmospheric Water is Continually Diluting Salt, and Eventually Overflows Container

Antimony trichloride
Mercuric nitrate
Sodium sulfide, nonahydrate
Trichloroacetic acid
Zinc chloride.

Self-Pressurizing

Chloroformate esters
Chromic acid (spent)
Diethyl pyrocarbonate
Formic acid
Methyl formate
Methyl ethyl ketone peroxide in dimethyl phthalate
Hydrogen peroxide solution
Pyruvic acid
Trichloromethyl carbonate

TOXIC GAS GENERATION

Certain compounds when mixed, as in a spill or breakage in a package, can produce toxic gases. This danger is present when at least one component is a liquid or a dissolved solid, usually as an aqueous solution.

Compound	Mixed With	Produces
Ammonium Salts	Strong Base	Ammonia
Azide Salts	Strong Acid	Hydrazoic Acid
Bromide Salts	Strong Acid	Hydrogen Bromide
Bromide Salts	Strong Oxidizer	Bromine Vapor
Bromites or Bromates	Strong Acid	Bromine and Bromine Oxides
Chloride Salts	Strong Acid	Hydrogen Chloride
Chloride Salts	Strong Oxidizer	Chlorine Gas
Chlorite or Chlorate Salts	Strong Acid	Chlorine and Chlorine Oxides
Cyanide Salts	Any Acid	Hydrogen Cyanide
Ferrocyanide or Ferricyanide Salts	Strong Acid	Hydrogen Cyanide
Fluoride Salts	Strong Acid	Hydrogen Fluoride
Hypochlorite Salts	Any Acid	Chlorine
Iodide Salts	Strong Acid	Hydrogen Iodide
Methyl, Nitroso Amides (Diazald)	Any Base	Diazomethane
Nitrite Salts	Strong Acid	Nitric Oxides
Sulfide or Bisulfide Salts	Any Acid	Hydrogen Sulfide
Sulfite or Bisulfite Salts	Any Acid	Sulfur Dioxide