

The Waste-Paper

The Hazardous Waste Disposal Monthly Update

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Time-Sensitive Chemicals Part 1

This is the first in a series of articles about chemicals that, when stored for prolonged periods, can develop hazards that were not present in the original formulation. Some of these additional hazards develop from inappropriate storage conditions, e.g. sunlight, heat, while others develop simply from storing the chemicals too long.



Peroxide Forming Chemicals

Peroxide crystals in ethyl ether

The most commonly encountered time-sensitive chemicals are those that form peroxides on exposure to air and light. Since they are sometimes packaged in an atmosphere of air, peroxides can form even though the containers have not been opened. Peroxides may detonate with extreme violence when concentrated by evaporation or distillation, when combined with other compounds, or when disturbed by unusual heat, shock or friction. Formation of peroxides in ethers is accelerated in opened and partially emptied containers. **Refrigeration will not prevent peroxide formation and stabilizers will only retard formation.**

Peroxide formation may be detected by visual inspection for crystalline solids or viscous liquids, or by using chemical methods or specialized kits for quantitative or qualitative analysis. **If you suspect that peroxides have formed, do not open the container to test since peroxides deposited on the threads of the cap could detonate.**

Even shiny, metal cans of ether may have peroxide-formation. In the U.S., there have been numerous incidents where even trained hazardous materials specialists have had containers of peroxide-forming chemicals detonate upon unscrewing the cap or even tipping the container.

Recommendations for Peroxide-Formers

- Label containers with the date received, the date first opened and the date for disposal as recommended by the supplier.
- Minimize peroxide formation in ethers by storing in tightly sealed containers placed in a cool place in the absence of light. Do not store ethers at or below the temperature at which the peroxide freezes or the solution precipitates.
- Choose the size container that will ensure use of the entire contents within a short period of time.

- Do not use solutions of peroxides in volatile solvents under conditions in which the solvent might be vaporized. This could increase the concentration of peroxide in the solution.
- Do not use metal spatulas or magnetic stirring bars (which may leach out iron) with peroxide forming compounds, since contamination with metals can lead to explosive decomposition. Ceramic, Teflon or wooden spatulas and stirring blades are usually safe to use.
- Do not use glass containers with screw-top lids or glass stoppers. Polyethylene bottles with screw-top lids may be used.

The following are the most common peroxide forming chemicals, along with their recommended maximum storage times:

Peroxide Hazard on Storage: Discard After Three Months

Divinyl acetylene	Potassium metal
Divinyl ether	Sodium amide
Isopropyl ether	Vinylidene chloride

Peroxide Hazard on Concentration: Discard After One Year

Acetal	Ethylene glycol dimethyl ether (glyme)
Cumene	Furan
Cyclohexene	Methyl acetylene
Cycloxyene	Methylcyclopentane
Cyclopentene	Methyl isobutyl ketone
Diacetylene	Tetrahydronaphthalene (Tetralin)
Dicyclopentadiene	Tetrahydrofuran
Diethyl ether	Vinyl ethers
Diethylene glycol dimethyl ether (diglyme)	
Dioxane	

Hazardous Due to Peroxide Initiation of Polymerization*: Discard After One Year

Acrylic acid	Styrene
Acrylonitrile	Tetrafluoroethylene
Butadiene	Vinyl acetylene
Chloroprene	Vinyl acetate
Chlorotrifluoroethylene	Vinyl chloride
Methyl methacrylate	Vinyl pyridine

Take advantage of the monthly pickups to minimize potential hazards. For more information, see the [Lab Safety Manual](#) or contact EHS.

Where’s all of our hazardous chemical waste going?



Many of us would be surprised by the answer. The hazardous waste industry has evolved significantly since its inception some 30 years ago. Our waste contractors, Triumvirate Environmental and Clean Harbors, Inc., do all they can to make disposal of hazardous chemical waste environmentally sound.

By far, the most significant innovations have come from the use of flammable liquid waste in “fuel blending.” In 2005 Princeton University generated nearly 4,000 gallons of flammable liquid waste including halogenated/non-halogenated solvent waste from laboratory research as well as solvent-based paint and thinners from Facilities. The major outlet for our flammable liquid “fuel” is the cement manufacturing industry. Cement manufacturing is a tremendously energy-intensive process. In 1970, the cement kiln industry burned nearly 1.6 billion liters fuel oil and nearly 6 billion cubic meters of natural gas. By 2000, through offsets resulting primarily from the use of alternative fuels the industry had reduced its consumption to 0.124 billion liters of fuel oil and just over 1 billion cubic meters of natural gas.

Wastes that are candidates for fuel blending are somewhat a select group. Therefore it is extremely important that other wastes not be combined with a laboratory’s flammable liquid wastes. We have been battling a rash of “off specification” carboys (e.g., low or high pH) of organic solvents. The combining of corrosives with flammable liquid wastes eliminates the opportunity for using the waste as a fuel. So, if possible, don’t combine corrosive waste with flammable liquid wastes.

The recycling of elemental mercury is another way EHS is reducing the University’s production of hazardous waste. Mercury is collected, even removed from devices such as manometers and gauges, into a steel shipping flask. When full, the flask is shipped to a mercury retort facility where it is purified and collected. The resulting material is shipped for reuse in other mercury containing devices. This is an extremely important activity as mercury is one of the most persistent environmental contaminants in the world today. Another recycling alternative to disposal is the remediation of compressed gas cylinders. EHS recently sent 95 gas cylinders to Chemical Analytics, Inc., a company specializing in compressed gas cylinder management. Chemical Analytics was successful in finding new end-users for the remaining gas inventories. Obviously it is much better from an environmental standpoint when a would-be waste material can be re-used rather than incinerated

Although there remain several wastes generated on campus that have no alternative disposal option, EHS and its waste contractors are always working to minimize the quantity of hazardous waste sent for destruction.

If you have any questions about the EHS effort to optimize hazardous waste disposal contact Steve Elwood at (selwood@princeton.edu) or 8-6271.

*Please bring waste
down to your Collection
site on
Wednesday, March
29th
Waste Pickup will be
Thursday,
March 30, 2006.*

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