Safety Alert

Issued 2014

Dangers of prolonged storage of ‘time sensitive’ chemicals

When stored for long periods of time, some chemicals develop additional hazards that were not present in their original formulation. Such chemicals are known as ‘time sensitive’ chemicals.

These chemicals, even when under normal storage conditions decompose to form *peroxides* that are extremely flammable and sometimes explosive. In the decomposed phase, they present a significant hazard to chemical users, infrastructure and the environment. For these reasons, time sensitive chemicals have *a limited shelf life*. If these chemicals are managed appropriately, they pose no additional risk beyond those identified in their safety data sheets.

Issue

A science operations officer identified potentially explosive peroxide crystals around the lids of several bottles of chemicals located in a storeroom. The information on the labels identified the chemical as diethyl ether and indicated that it was purchased in 1993.

Diethyl ether is a known peroxide former. It has an unopened shelf life of 18 months and a usage (opened) shelf life of 12 months. Because hazardous peroxides pose an explosive hazard, it was necessary for emergency services to attend the school. They determined that because of its age and condition, the ether posed an unacceptably high safety risk. The chemicals were disposed of onsite using controlled ignition so as to avert any potentially serious future event.

Corrective actions

- Dispose of **opened** container of diethyl ether **12 months** after date received (unless tested as peroxide free).
- Dispose of **unopened** containers of diethyl ether after **18 months** from the date of manufacture.

Schools can avoid such scenarios by disposing of time sensitive chemicals when they reach the end of their shelf life. There is no value in holding on to expired or unused chemicals – the potential safety risks are too great.

Where to start – identifying peroxides

1. Identify all known peroxide-forming compounds in your storage areas.
2. Establish a laboratory routine to test these chemicals at a set time (e.g. on the first day of each month) or no later than every three months.
3. Keep a register of these compounds and test and log results according to established schedules. If suspect crystals are recognised, do not handle the container.
    a. Never test containers that do not pass visual inspection.
    b. Never test containers of unknown age or origin. Dispose of these containers according to process below.

For liquid chemicals: some liquids form a peroxide hazard on concentration e.g. *diethyl ether, cyclohexene, sec-butyl and t-butyl alcohol, 3-Methyl-1-butanol, 2-Propanol*. Secondary alcohols (e.g. *2-butanol*) may also form peroxides when distilled, evaporated or otherwise concentrated.

- Inspect for water content, discoloration, crystal deposits on the walls (inside or outside), white residue around the neck or cap or a 'mossy' appearance around the neck of the bottle. For amber glass, it may be useful to backlight the inspection with a battery powered torch.
- Dispose of no later than **12 months from opening** or **three years from date of manufacture** (excl. diethyl ether) if unopened. Refer to the product's safety data sheet for disposal advice.

For solid chemicals: some solids form a peroxide hazard on storage – they spontaneously decompose and become explosive with air without being concentrated e.g. *potassium metal, sodium amide*.

- Look for discolouration and/or formation of a yellow to orange coating of superoxide. The coating can explode or catch fire upon cutting.
- Even when these metals are stored under mineral oil, oxygen can dissolve in the oil and cause oxidation. Evaluation of peroxides in alkali metals and their amides is based on visual inspection only (no testing).
- Dispose of **three months after date opened** (unless peroxide free). Dispose of **one year** after date received (**unopened**). Refer to the product's safety data sheet for disposal advice.

What to do with suspected or known peroxides

Any container with visible discolouration, crystallisation or liquid stratification should be treated as potentially explosive.

1. Do not open or test containers of unknown age or origin or that have visible evidence of peroxides. Older containers pose far greater potential risk of containing crystallised peroxides inside the cap thread. The friction of unscrewing the cap could detonate the bottle with disastrous results. Heat or mechanical shock may also cause detonation. Older solvent containers made of steel or with rusty metal lids may also be particularly dangerous
2. Eliminate all sources of ignition and secure the location to prevent unauthorised entry.
3. Advise school staff of the situation; (HOD, principal and health and safety advisor). The school should then promptly contact its regional health and safety consultant for immediate disposal advice https://education.qld.gov.au/initiatives-and-strategies/health-and-wellbeing/workplaces/contacts.

What to do with *other* time sensitive chemicals

- **Picric acid** (when dry) is an extremely high risk peroxide former. If you have picric acid, contact your regional health and safety consultant for assistance with immediate disposal. The hazards posed by this chemical inherently exceed its educational value in the school curriculum.
- **Chloroform** (on contact with air) decomposes to form highly toxic phosgene gas. Dispose of open bottles after three months, otherwise two years from the date of manufacture.
- **Methyl Ethyl Ketone Peroxide** (MEKP) is shock sensitive. It also gradually decomposes during storage in sealed containers which may lead to a large pressure build-up and subsequent explosion. Shelf life is three months at 25°C. Similarly, **formic acid** is to be disposed of after 12 months due to the risk of pressure build-up in the container. Point these containers away from the face when opening them.

Cylinders containing **corrosive gas** are to be returned to the manufacturer after two years from receipt.

Good laboratory practice for the safe storage of time sensitive chemicals

How do I test for peroxides?

1. Test only if the container passes visual inspection.
2. The most efficient method* is to use commercial test strips that use a colourmetric scale (available from most science suppliers). The control threshold for peroxides is 100ppm. A strip range of 1-100 ppm is useful to determine if the material is below the threshold. < 25 ppm is considered safe for general use.
    - >100 ppm avoid handling and contact your Regional Consultant for immediate assistance with safe disposal. DO NOT dispose of by evaporation as this may accelerate peroxide formation.
    - Test known peroxidisable chemicals for peroxides *each time* before any distillation, purification or heating process is used. Do not use if peroxides >25 -100 ppm.
    - Chemicals which are older than the suggested shelf life but have no detectable peroxides or peroxide concentrations less than 100 ppm may be retained BUT are to be tested at frequent intervals.

Management of time sensitive chemicals

1. Purchase the smallest quantity that is practical for all time-sensitive chemicals. Substitute with less hazardous materials where possible; otherwise purchase time-sensitive stock that is manufactured with stabilisers (e.g. BHT).
2. Peroxides tend to form in materials as a function of age. Therefore, you must be aware of the age of any peroxide-forming chemicals. Enter the chemical into your inventory as soon as possible and label each container with date received, date opened and date last tested. Do the same for decanted containers as soon as they are filled. Store and test as for parent stock.
3. Use your peroxide register to track time sensitive chemicals and test results.
4. Store peroxidisable substances in original containers according to the SDS and dispose of promptly according to shelf life characteristics. Peroxides can also build up over time as solvent evaporates and/or air seeps into the bottle or if the bottle is opened and closed frequently.
5. Line managers are to be aware of the risks associated with time sensitive chemicals to enable appropriate support and resources to be provided to workers to safely manage these products.

---

*Other laboratory detection methods are discussed in *Guidelines for Explosive and Potentially Explosive Chemicals Safe Storage and Handling*, Berkley University http://www.ehs.berkeley.edu/sites/default/files/lines-of-services/hazardous-materials/pecguidelines.pdf.