FactSheet Peroxide-Formers

Many chemicals slowly react with atmospheric oxygen during storage, causing a build-up of peroxides; i.e., compounds containing O-O bonds. Peroxides are generally oxidizing, unstable, and may ignite or explode on slight disturbance. Peroxide build-up has been the direct cause of many serious and even fatal accidents.

Peroxide-formers are grouped into classes based on their hazard (see back page). Commercial organic compounds susceptible to peroxide formation (especially solvents) may be supplied with a free-radical inhibitor (stabilizer) which will markedly slow peroxidation in storage. When the inhibitor is completely consumed with time, however, peroxidation will form unstable peroxide compounds.

Visible indicators of potentially severe peroxide contamination:

- Solid precipitate in a peroxidizable organic liquid
- Incrustation around cap
- Second liquid phase
- Visible discoloration
- Rusty or excessively old containers of peroxide-forming compounds

STOP

- Do not attempt to move or open suspect containers.
- Warn co-workers and supervisors of hazard.
- Restrict access to surrounding area.
- Call EH&S immediately.

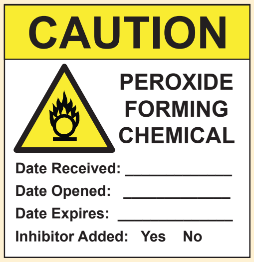
Recommended Practices Include:

- Purchase and use stabilized solvents where possible. Note that stabilizers are removed by distillation or adsorption (e.g., on activated alumina or silica gel).
- Use unstabilized solvents immediately after opening. Add a stabilizer or de-aerate and store under inert atmosphere.
- Distillation or evaporation will concentrate peroxides; distill only fresh material. **Do not distill to dryness.**
- Peroxidation is greatly accelerated by light especially in the presence of trace photosensitizers (e.g., ketones). **Store in an amber bottle and/or in the dark.**
- Test solvents/materials frequently for the presence of peroxides.

Peroxides can also be formed by the reaction of hydrogen peroxide with organic solvents, particularly ketones. Even in the absence of overt peroxide formation, hydrogen peroxide of sufficient concentration (30% or greater) may form redox mixtures with organic materials that can potentially detonate.

Labelling and Inventory Control

- Label and date all peroxidizable materials using the label illustrated below. Labels are available from EH&S.
- Operate a "first-in, first-out" inventory system and only have one opened container at any time. Keep inventory at a minimum especially for Class A materials.
- If conducting regular peroxide tests, attach a log of dates and test results to bottle. Notify EH&S for disposal when concentrations approach 100 ppm.



CAUTION

PEROXIDE FORMING CHEMICAL

Date Received: ____________
Date Opened: ____________
Date Expires: ____________
Inhibitor Added: Yes No

Besides organic peroxide-formers, there are a limited number of inorganic compounds which display analogous hazards. During storage, potassium grows an oxidizing crust which may inflame or explode on disturbance. After minimal air exposure potassium amide and sodium amide subsequently become unstable and may spontaneously ignite or explode, with no visual indication to warn of the danger.

TESTING AND REMOVAL OF ORGANIC PEROXIDES

There are published procedures for testing for the presence of organic peroxides, but the tests are principally sensitive to hydroperoxides and may underestimate the presence of other peroxo-constituents. Refer to the literature and to manufacturers data on peroxide test kits for details on appropriate usage.

There are procedures for remediating moderately peroxidized (<1000 ppm) organic liquids; however, all have limitations and require chemistry expertise to conduct safely. Please consult Kelly (1996) and other sources for details. If in doubt, dispose via EH&S rather than attempting remediation.

Do not rely on refrigeration to slow peroxidation. As reports indicate, this may have no effect or may even promote peroxide build-up by slowing the decomposition of unstable peroxides.

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MATERIAL	MAXIMUM STORAGE PERIODS
Unopened container from manufacturer	6 months for Class A materials, generally 18 months for others; check manufacture's information
Opened Class A	3 months (except potassium metal, see below)
Opened Class B	12 months. If uninhibited, either store under N2 or test for peroxides on a regular schedule.
Uninhibited Class C	24 hours max, small quantities only
Inhibited Class C	12 months in air (unless also in Class A, when 3 month period applies). Do NOT store under inert atmosphere, as the polymerization inhibitor may only work in the presence of oxygen.
Potassium metal	Highly variable ageing depending on storage conditions. Visually check for crusting every 3 months.

CLASS A
Peroxide-Formers

The most hazardous materials, which can develop dissolved peroxide concentrations high enough to directly constitute a mass explosion hazard, or which can deposit concentrated peroxides as a solid or second liquid phase. Diisopropyl ether is especially notorious, and should never be used as a solvent.

- Butadiene (liquid)
- Chloroprene (liquid)
- Diisopropyl ether
- Divinylacetylene
- Potassium amide
- Potassium metal (and NaK)
- Sodium amide (sodamide)
- Tetrafluoroethylene (liquid)
- Vinylidine chloride

CLASS B
Peroxide-Formers

Class B materials readily form peroxides, but the peroxide concentration is low enough (< ca. 1%) for the solution to not be a mass explosion hazard. However, any operation involving evaporation will concentrate the peroxides in the residue, which may become dangerously explosive.

- Acetaldehyde
- Benzyl alcohol
- Benzyl ethers
- Bis(2-methoxyethyl) ether (diglyme)
- 2-Butanol
- Cumene
- Cyclohexene
- Decahydronaphthalene (decalin)
- Dicyclopentadiene
- Diethyl ether
- Dioxane(s)
- 1,1-Diethoxyethane (acetal)
- Furan
- Methyl isobutyl ketone
- Tetrahydrofuran (THF)
- 1,2-Dimethoxyethane (glyme)
- Tetrahydronaphthalene (tetralin)
- Vinyl ethers
- Other secondary alcohols

CLASS C
Peroxide-Accumulation May Initiate Uncontrolled Exothermic Polymerization

Especially dangerous when uninhibited—store only in the stabilized form. Condensate forming above the liquid level in bottles is inhibitor free, and may polymerize and block the bottle. Storage of stabilized materials under inert atmosphere may induce uncontrolled polymerization!

- Acrylic acid
- Acrylonitrile
- Butadiene (gas)
- Chloroprene (gas)
- Chlorotrifluoroethylene
- Methyl methacrylate
- Styrene
- Tetrafluoroethylene (gas)
- Vinylacetylene
- Vinyl acetate
- Vinyl chloride
- Vinylidine chloride
- Vinylpyridine

CLASS D
Other Known and Suspected Peroxide Formers

All compounds containing C-H groups activated towards radical reactions are potentially susceptible to peroxidation, although whether peroxides will decompose as fast as they are formed or accumulate to dangerous levels is hard to predict. In approximate order of decreasing danger, known susceptible compounds include the following:

- Ethers and acetals
- Alkenes with allylic-H
- Chloro- and fluoroalkenes
- Vinyl halides and esters
- Dienes
- Vinylalkynes
- Alkylalkynes
- Alkylarenes with tertiary α-H
- Alkanes/cycloalkanes with tertiary-H
- Acrylates, methacrylates
- Secondary alcohols
- Ketone
- Aldehydes
- Ureas/amides/lactams with N-C-H moiety

FURTHER INFORMATION:

[1] Kelly, R. J. Review of Safety Guidelines for Peroxidizable Organic Compounds. Chemical Health and Safety 1996 (Sept./Oct.), 28-36. (Easily findable in pdf format via online search.)

[2] Numerous entries, including "Peroxides in Solvents", "Peroxidisable Compounds", and "Peroxidation Incidents", plus entries on individual compounds: Bretherick's Handbook of Reactive Chemical Hazards, 7th ed. (Available online through USC subscription at www.knovel.com.)