Peroxide Forming Solvents

A significant number of laboratory solvents can undergo autoxidation under normal storage conditions to form unstable and potentially dangerous peroxide by-products. This process is catalyzed by light and heat and occurs when susceptible materials are exposed to atmospheric oxygen. Molecular structure is the primary factor relating to a material’s potential for hazardous peroxide formation.

Most overviews of potential peroxide-forming chemicals classify various materials into three categories, on the basis of peroxide formation susceptibility, each with general handling and use guidelines.1 The two categories relevant to solvents are defined as solvents that pose a peroxide related safety risk without having to be pre-concentration (see Group A, next section) and solvents that necessitate pre-concentration in order to form peroxides (see Group B, next section). Storage time guidelines for previously opened containers is provided in the section following this paragraph (Potential Peroxide-Forming Solvents*). Please note that the storage time indicated below are based on these solvents continually being stored in opaque containers and under inert atmospheric gases.

Potential Peroxide-Forming Solvents*

**Group A:** Chemicals that form explosive levels of peroxides without concentration
Severe peroxide hazard after prolonged storage, especially after exposure to air.
*Test for peroxide formation before using or discard after 3 months.*
- Isopropyl ether
Group B: Peroxide hazards on concentration

Test for peroxide formation before distillation or evaporation. Test for peroxide formation or discard after 1 year.

- Acetal
- Acetaldehyde
- Benzyl Alcohol
- 2-Butanold Dioxyanese
- Chlorofluoroethylene
- Cumene(isopropylbenzene)
- Cyclohexene
- 2-Cyclohexen-1-ol
- Cyclopentene
- Decahydnaphthalene(dcalin)
- Diacetylene(butadiyne)
- Dicyclopentadiene
- Diglyme
- Diethyl ether
- Ethylene glycol ether acetates
- Furan
- 4-Heptanol
- 2-Hexanol
- Methyl Acetylene
- 3-Methyl-1-butanol
- Methylisobutyl ketone
- 4-Methyl-2-pentanol
- 2-Pentanol
- 4-Penten-1-ol
- 1-Phenylethanole
- Tetrahydrofuran
- Tetrahydronaphthalene
- Vinyl Ethers
- Sec. Alcohols

* Materials other than those listed may form peroxides. Applies only to pure materials.

Use and Storage of Peroxide-Forming Solvents

The solvents most commonly used in the laboratory solvents, such as diethyl ether, tetrahydrofuran, cyclohexene, glycol ethers, decalin and 2-propanol are shown in Group B of the previous section. These compounds produce organic peroxides that are significantly less volatile than the solvent in which they are formed, as a result, evaporative concentration or distillation can produce dangerous levels of peroxides. In fact, most Group
B solvents are sufficiently volatile that multiple openings of a single container can result in significant and dangerous peroxide concentration. The next section contains a list of key aspects to consider when handling peroxide-forming solvents.

**General Handling Considerations for Peroxidizeable Solvents:**

- All peroxide-forming solvents should be checked for the presence of any peroxides prior to distillation or evaporation.
- Solvents containing low levels of free radical scavengers such as BHT should be used whenever the presence of the stabilizing species does not interfere with intended application.
- Uninhibited materials should be stored with care and frequently checked for peroxide formation.
- Peroxide-forming solvents should be purchased in limited quantities and older material in inventory should be preferentially selected for use.
- Materials should be stored away from light and heat with tightly secured caps and labeled with dates of receipt and opening.
- Periodic testing to detect peroxides should be performed and recorded on previously opened material.

For more information, it is recommended that the reader review the articles referenced below by Kelly\(^2\) and/or Clark\(^3\)

**Peroxide Detection**

A variety of methods are available to test for the presence of peroxides in organic solvents with the two most common tests described below. At present, 100 ppm is widely used as a general control point with respect to minimum hazardous peroxide concentration in a solvent, however, this value lacks scientific validation and is likely too liberal or conservative depending on the solvent in question and intended application.\(^2\) If there are visible crystals, visible precipitate or an oily viscous layer present in the material, these are visual indicators of
dangerous high peroxide levels, immediately contact your company’s EH&S (Environmental, Health and Safety) department or its equivalent, to manage this hazardous situation and to dispose of this material.

**Quantofix® Peroxide Test Strips (Sigma-Aldrich Part # 37206)**

In the presence of hydrogen peroxide the test paper turns blue. Quantofix® Peroxide test sticks can also be used for the determination of peracetic acid and other organic and inorganic hydroperoxides. To test for hydroperoxides in organic solvents, the test zone is wetted with one drop of water after evaporation of the solvent.

**Interferences:** In the pH range of 2-9, the accuracy of the determination is independent of the pH of the test solution. Buffer strongly acidic solutions with sodium acetate and adjust alkaline solutions to about pH 5-7 with citric acid. Falsely positive results can only be caused by strong oxidizing agents.

**Storage:** Avoid exposing the sticks to sunlight and moisture. Store unopened packs in refrigerator (+2 °C to +8 °C). Opened packs: store container in a cool and dry place.

**Potassium Iodide Indicator**

Add 0.5-1.0 ml of the sample solvent to an equal volume of glacial acetic acid containing about 0.1 g of sodium iodide or potassium iodide crystals. A yellow color indicates iodine formation via iodide oxidation by sample peroxide; a brown color indicates high concentration. A blank determination should be made particularly when color development is faint since iodide/acetic acid mixtures will, over time, turn a yellow - brown
color due to air oxidation.

A more sensitive variation of the above method adds one drop of a saturated, aqueous starch solution to the sample solution. Starch and iodine combine to form a bright blue complex that is more easily visualized than the yellow color generated by iodine alone. Dark blue solution color would be indicative of high peroxide concentrations.

References