

Peroxide Forming Chemicals

Standard Operating Procedure

Revision Date: 05/16/22

## Laboratory Director (LD) Approval is Required Prior to Performing this Procedure

### Description [Provide additional information as it pertains to your research protocol]

This standard operating procedure (SOP) outlines the handling and use of peroxide forming chemicals. Review this document and supply the information required in order to make it specific to your laboratory. In accordance with this document, laboratories should use appropriate controls, personal protective equipment, and disposal techniques when handling peroxide forming chemicals.

Due to the inherent risks associated with prolonged storage of peroxide forming chemicals, experiments and processes should be planned appropriately so that only the quantities necessary are procured.

Prolonged storage in the lab should be avoided. If peroxide forming chemicals will be stored in the lab, the storage needs and testing requirements for each one must be specified in the “Process” section of this SOP.

***Process [Write the storage/testing requirements and steps for using the chemical in your research protocol]***

**Potential Hazards [Provide additional information as it pertains to your research protocol]**

## Peroxide Formation

Peroxide formation in common laboratory chemicals is caused by an autoxidation reaction. The reaction can be initiated by light, heat, introduction of a contaminant, oxygen or the loss of an inhibitor. Some chemicals have inhibitors such as BHT (butylated hydroxytoluene), hydroquinone, and diphenylamine to slow peroxide formation. Most organic peroxide crystals are sensitive to heat, shock, or friction, and their accumulation in laboratory reagents has resulted in numerous explosions. In addition, some chemicals will autopolymerize as a result of peroxide accumulation. Autopolymerization can result in a rapid temperature rise, leading to overpressurization and catastrophic container failure. For these reasons, it is important to identify and control chemicals that form potentially explosive peroxides.

## Peroxide Forming Compounds

In general, the more volatile the compound, the greater its hazard, since the evaporation of the compound allows the peroxide to concentrate. Peroxide accumulation is a balance between peroxide

formation and degradation. Peroxide forming chemicals should be used or disposed of prior to the expiration date. If extenuating circumstances exist for keeping the chemical, routine testing must be performed. ***\*\*\*Never open or test containers of unknown origin or age, or those that have evidence of peroxide formation.\*\*\****

Refer to the tables below for some common peroxide forming chemicals and testing frequencies. **The tables are non-exhaustive - review each material’s SDS to determine if a chemical can form peroxides, and to check for other hazards.**

**Useful Peroxide Forming Materials Links:**

* MSDS Hyper Glossary: <http://www.ilpi.com/msds/ref/peroxide.html>
* UC Berkeley incident report:

<https://ehs.berkeley.edu/lessons-learned/lesson-learned-peroxide-explosion-injures-campus-researcher>

* Peroxides and peroxide-forming compounds. D.E. Clark. 2001. Chemical Health and Safety, 8:12-22
* Cameo Chemicals <https://cameochemicals.noaa.gov/>

**NOTE**: **Tables 1 and 2 are not an exhaustive list of peroxidizable chemicals**. Users **must** consult the chemical’s [SDS](http://oseh.umich.edu/research-clinical-safety/chemical/safety-data-sheets/) and/or other sources of information for the chemicals used (and stored) in the lab to determine their peroxide-forming potential.

## Table 1 - Peroxidizable Chemicals Lists

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| **List A: Chemicals that form explosive levels of peroxides without concentration****Testing Frequency: 3 months** |
| **Chemical Name** | CAS # | Formula | Synonyms |
| **Butadiene1** | 106-99-0 |  | *Pyrrolene**Vinylethylene* |
| **Chloroprene1** | 126-99-8 | C4H5Cl | *Chlorobutadiene* |
| **Divinyl Acetylene** | 821-08-9 | H2C=CHCCCH=CH2 | *1,5-hexadien-3-yne* |
| **Isopropyl Ether** | 75-35-4 | C2H2Cl2 | *Diisopropyl ether**Diisopropyl oxide* |
| **Tetrafluoroethylene** | 116-14-3 |  | *Perfluoroethylene* |
| **Vinylidene Chloride** | 75-35-4 | C2H2Cl2 | *1,1-dichloroethylene**1,1-dichloroethene* |

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| **List B: Chemicals that form explosive levels of peroxides on concentration Testing Frequency, Inhibited: 12 months****Testing Frequency, Uninhibited: 3 months** |
| **Chemical Name** | CAS # | Formula | Synonyms |
| **Acetal** | 105-57-7 | C6H14O2 | *Diethylacetyl**ethylidene diethyl ether* |
| **Acetaldehyde** | 75-07-0 | C2H4O | *ethyl aldehyde**ethanal* |
| **Benzyl alcohol** | 100-51-6 | C7H8O | *Hydroxytoluene**Phenyl carbinol* |
| **2-Butanol** | 78-92-2 | C4-H10-O | *Sec-butyl alcohol* |
| **Cumene** | 98-82-8 | C9H12 | *Isopropyl benzene* |
| **Cyclohexene** | 110-83-8 | C6-H10 | *Tetrahydrobenzene* |
| **Cyclooctene** | 931-88-4 | C8H14 |  |

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| **Decahydronapthalene1** | 91-17-8 | C10H18 |  |  | *Decalin**DeKalin* |
| **Diallyl Ether** | 557-40-4 | C6H10O |  |  | *Propenyl ether* |
| **Dibenzyl Ether** | 103-50-4 | C14H14O | *Benzyl ether* |
| **Dicyclopentadiene** | 77-73-6 | C10H12 |  |  | *DCPD* |
| **Diethoxymethane** | 462-95-3 | C5H12O2 |  |  | *Formaldehyde diethyl acetal**Methylene glycol diethyl ether* |
| **Diethyl ether** | 60-29-7 | C4H10O |  |  | *Ethyl ether* |
| **Diethylene glycol Dimethyl ether** | 111-96-6 | C6H14O3 |  |  | *Diglyme**Dimethyldigol* |
| **1,2-Dimethoxyethane** | 110-71-4 | CH2(OCH3)2 | *Ethylene glycol dimethyl ether**EGDME**Glyme* |
| **1,4-Dioxane** | 123-91-1 | C4H8O2 |  |  | *Diethylene ether* |
| **4-Heptanol** | 589-55-9 | C7H16O |  |  |  |
| **2-Hexanol** | 626-93-7 | C10H18O2 | *Butyl methyl carbinol* |
| **Isoamyl alcohol** | 123-51-3 | (CH3)2CHCH2CH2OH | *3-Methyl-1-butanol*Isopentyl alcohol |
| **Isoamyl benzyl ether** | 122-73-6 | C12H18O |  |  | *benzyl isopentyl ether* |
| **Isoamyl ether** | 544-01-4 | C10H22O |  |  | *Isopentyl ether**Isoamyl oxide* |
| **Isophorone** | 78-59-1 | C9H14O |  |  | *Bisol Isophorone* |
| **Isopropanol2** | 67-63-0 | C3H8O |  |  | *2-propanol* |
| **p-Isopropoxypropionitrile** | 110-47-4 | C6-H11-N-O | *beta-**isopropoxypropionitrile* |
| **Isopropyl glycidyl ether** | 4016-14-2 | C6H12O2 |  |  | *1,2-Epoxy-3-isopropoxy**propane* |
| **Methyl isobutyl carbinol** | 108-11-2 | C6-H14-O |  |  | *4-methyl-2-pentanol**Methyl amyl alcohol* |
| **Methyl isobutyl ketone** | 108-10-1 | CH3COCH2CH(CH3)2 | *Isopropylacetone MIBK**4-methyl-2-pentanone* |
| **Methylal** | 109-87-5 | C3-H8-O2 |  |  | *Dimethoxymethane**Methylene dimethyl ether* |
| **Methylcyclopentane** | 96-37-7 | C6H12 |  |  |  |
| **1-pentene** | 109-67-1 | CH3(CH2)2CH=CH2 | *Propyl ethylene* |
| **4-Penten-1-ol** | 821-09-0 | C5-H10-O |  |  | *4-pentenol-1* |
| **Phenethyl alcohol** | 60-12-8 | C8H10O |  |  | *2-phenylethyl alcohol**Benzyl carbinol Benzylmethanol* |
| **Sec-phenylethyl alcohol** | 98-85-1 | C8-H10-O |  |  | *1-Phenylethanol* |
| **Tetrahydrofuran** | 109-99-9 | C4H8O |  |  | *Diethylene oxide**Furanidine* |
| [**Tetrahydronaphthalene**](https://www.google.com/search?es_sm=122&biw=944&bih=967&q=CAS%2B%23%2BTetrahydronaphthalene&spell=1&sa=X&ved=0CBoQvwUoAGoVChMI6ffFnJihxwIVCL9yCh1Saga-) | 119-64-2 | C10-H12 |  |  | *Tetralin**Tetranap* |

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| **List C: Chemicals that may autopolymerize as a result of peroxide accumulation****Testing Frequency, Inhibited: 12 months Testing Frequency, Uninhibited: 24 hours***\*\*Inhibited chemicals must not be stored under inert atmosphere. Oxygen is required for inhibitor to function\*\** |
| **Chemical Name** | CAS # | Formula | Synonyms |
| **Acrylic Acid** | 79-10-7 | C3H4O2 | *2-propenoic acid Vinylformic acid**Acroleic acid* |
| **Acrylonitrile** | 107-13-1 | C3-H3-N | *Vinyl cyanide**Carbacryl* |
| **Butadiene1**(also appears in List A) | 106-99-0 |  | *Pyrrolene**Vinylethylene* |
| **Chloroprene1**(also appears in List A) | 126-99-8 | C4H5C | *Chlorobutadiene* |
| **Methyl Methacrylate** | 80-62-6 | C5H8O2 | *2-propenoic acid*, *2- methyl methyl ester methyl alpha**methacrylate* |
| **Styrene** | 100-42-5 | C6H5CH=CH2 | *vinyl benzene**phenylethene* |
| **Tetrafluoroethylene**(also appears in List A) | 116-14-3 |  | *Perfluoroethylene* |
| **Vinyl Acetate** | 108-05-4 | H2C=CHOOC-CH3 | *Ethenyl ethanoate**Acetic acid vinyl ester* |
| **Vinyl Chloride** | 75-01-4 | C2H3Cl | *Chloroethylene**Chloroethene* |
| **Vinylidene chloride**(also appears in List A) | 75-35-4 |  | *1,1-dichloroethylene**1,1-dichloroethene* |
| **2-Vinyl Pyridine** | 100-69-6 | C7-H7-N |  |
| **4-Vinyl Pyridine** | 100-43-6 | C7-H7-N |  |

1. When stored in liquid form these chemicals may form explosive levels of peroxides without concentration. When stored as a gas, these chemicals may autopolymerize as a result of peroxide accumulation.
2. 2-Propanol does not need to be routinely tested if only used for cleaning or other activities where it will not be distilled or otherwise concentrated.

Table 2 contains a partial list of solids, compressed gases and liquefied gases that will form peroxides. Since it is not possible to readily/easily test for the presence of peroxides in these materials, guidance is provided for suggested safe storage times.

## Table 2: Solids, Compressed Gases and Liquefied Gases That Will Form Peroxides

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| **Material** | **CAS****Chemical Formula** | **Storage Guidelines** |
| Potassium metal (Solid) | 7440-09-7 | If stored longer than 6 months to a year, dangerous shock- sensitive peroxides can form on the metal and under the lid of the container, which can detonate upon opening.It is recommended that potassium not be stored for longer than three months unless stored in an inert (oxygen-free) atmosphere, or under vacuum. |
| Sodium amide (Divided solid normallysupplied as a suspensionin toluene or xylene) | 7782-92-5H2NNa | Easily forms dangerous levels of unstable peroxides in storage. Discard within 3 months. |
| Butadiene(Compressed or liquefied gas) | 25339-57-5CH2=CHCH=CH2 | Butadiene and oxygen readily react to form thermally unstable butadiene peroxide.Follow guidance from supplier regarding safe storage timelines and expiration dates. |
| 1,3-Butadiene (Compressed or liquefied gas) | 106-99-0C4-H6 | Butadiene and oxygen readily react to form thermally unstable butadiene peroxide.Follow guidance from supplier regarding safe storage timelines and expiration dates. |
| Tetrafluoroethylene (Compressed or liquefiedgas) | 116-14-3C2-F4 | Spontaneously forms peroxides in contact with air.Follow guidance from supplier regarding safe storage timelines and expiration dates. |
| Methyl acetylene (Compressed or liquefiedgas) | 74-99-7C3-H4 | Follow guidance from supplier regarding safe storage timelines and expiration dates. |
| 1,3-Butadiyne (Compressed gas) | 460-12-8C4H2 | Follow guidance from supplier regarding safe storage timelines and expiration dates. |
| Chlorotrifluoroethylene (Liquified gas) | 79-38-9C2ClF3 | Follow guidance from supplier regarding safe storage timelines and expiration dates. |
| Buten-3-yne(Compressed gas) | 689-97-4C4H4 | Follow guidance from supplier regarding safe storage timelines and expiration dates. |

**Engineering Controls [Provide additional information as it pertains to your research protocol]**

Use a fume hood or other appropriate exhaust ventilation if inhalation hazard is anticipated. Utilize shields, barricades, and additional PPE (such as face shields with throat protectors and heavy gloves) where there is a possibility of explosion or vigorous chemical reaction.

**Work Practice Controls [Provide additional information as it pertains to your research protocol]**

* Whenever possible, avoid purchasing a volume of any peroxide forming chemical that cannot be reasonably used before the required test/disposal date.
* Purchase peroxide formers with inhibitors added by the manufacturer when possible.
* **Mark the container with the *date it was received* and *the date it was opened*. If tested for peroxides, note the date it was tested.**
* **Note:** some peroxide formers (including alkali metals and their amides) should not be tested with standard peroxide tests because they are both water and oxygen-reactive
* When numerous peroxide forming chemicals are present in an inventory, use a spreadsheet, list, or inventory management tool to keep track of PFCs and relevant dates.
* Do not use metal spatulas to handle peroxides because contamination by metals can lead to explosive decomposition. Magnetic stirring bars can unintentionally introduce iron, which can initiate an explosive reaction of peroxides. Ceramic, Teflon, or wooden spatulas and stirring blades may be used if it is known that the material is not shock-sensitive.
* Do not allow materials to evaporate to near dryness unless absence of peroxides has been shown.
* Periodically test containers with peroxide test strips. See testing section below for more information.

Contact EHS for assistance in performing an exposure assessment.

**Note: Never try to force open a rusted or stuck cap on a container of a peroxide-forming chemical.**

## Testing Procedures

There is a great deal of uncertainty regarding the concentration at which peroxides pose a hazard to researchers. Various sources suggest that the minimum hazardous concentration of peroxides in organic solution is in the range 0.005 - 1.0% (50-10,000 ppm). In most safety literature, a conservative concentration of 100 ppm peroxides is used as a control point.

By the end of the expiration date for a particular peroxide forming chemical, the person using the chemical should either dispose of it or test it for peroxide content.

Materials which are older than the suggested shelf life but have been tested and have no detectable peroxides may be retained but should be re-tested. ***All chemicals which are to be distilled must be tested prior to distillation regardless of age.***

**Important note: Researchers should never test containers of unknown age or origin. Older containers are far more likely to have concentrated peroxides or peroxide crystallization in the cap threads and therefore can present a serious hazard when opened for testing. Please read section below on managing older containers.**

There are several methods that are commonly used to detect for peroxides in the laboratory. Perhaps the most convenient method is the use of peroxide test strips that are manufactured by several companies. These strips are simple to use and can be obtained from a chemical supplier. Test methods for aqueous solutions and organic solvents vary by manufacturer so it is important to follow the instructions supplied with the strips purchased for use in the lab. A color change on the strip indicates the presence of peroxides. The color chart provided for comparison to determine the concentration of peroxides present should be considered a guideline only. In the event the strip does change color, the safest action is to contact EHS Hazardous Materials Management to have the chemical picked up for disposal. Should the lab desire to keep the chemical, additional specific tests for peroxides are available and will need to be utilized. Contact EHS at (734) 647-1143 for more information.

**Personal Protective Equipment [Provide additional information as it pertains to your research protocol]**

Wear standard nitrile laboratory gloves (or those recommended on the SDS), lab coat, and safety glasses or goggles (meeting the requirements of ANSI/ISEA Z87.1) for all work in the laboratory.

Also, refer to the Environment, Health & Safety (EHS) [Glove Compatibility Chart](http://ehs.umich.edu/research-clinical/planning-safe-research/glove-compatibility-chart/) Web page.

**Transportation and Storage [Provide additional information as it pertains to your research protocol]**

* Store in airtight containers in a dark, dry, and cool but not freezing area.
* Do not permit sources of heat, friction, grinding, or impact near storage areas.

### Date upon receiving and opening all incoming peroxide forming chemicals and dispose of or test them immediately upon reaching their expiration date.

* Some peroxide-formers should be stored under nitrogen (or other inert gas) – consult the chemical’s SDS for more information.

### Waste Disposal [Provide additional information as it pertains to your research protocol]

Most spent, unused and expired materials are considered hazardous wastes and **must be collected and disposed of within 90-days** by the EHS Hazardous Materials Management (EHS-HMM) Group. Contact EHS- HMM at (734) 763-4568 for waste containers, labels, manifests, waste collection and for any questions regarding proper waste disposal. Also, refer to EHS [Hazardous Waste](http://ehs.umich.edu/haz-waste/) Web page for more information.

Contact EHS-HMM ***immediately*** to arrange for pick-up and disposal if:

* No receipt date is found on the container and the age of the chemical is unknown.
* Crystals are found around the lid of the container. Do **NOT** attempt to open the container! or
* The container tests positive for peroxides.

# Training of Personnel

All personnel shall read and fully adhere to this SOP when handling peroxide forming chemicals.

# Certification

I have read and understand the above SOP. I have received approval from my Lab Director to perform this procedure. I agree to contact my Lab Director if I plan to modify this procedure.

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| **NAME** | **SIGNATURE** | **UMID #** | **DATE** |

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| Lab Director | Revision Date |

**Major Revisions (Tracking purposes only -- Do not print as part of SOP)**

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| **DATE** | **REVISION** |
| 09-19-18 | Updated EHS name and logo and format and revised the Exposure/unintendedcontact section (AKJ) |
| 03-18-19 | Updated links, certification and formatting (DML). |
| 05—04-20 | Updated links, formatting (LS) |
| 08-25-21 | Removed 2-methyl-1-butanol and added 3-methyl-1-butanol to List B chemicals in Table 1Added note that 2-Propanol does not need to be routinely tested if only used for cleaning and is not distilled or otherwise concentrated (LS) |
| 11-09-21 | Updated guidance regarding testing for peroxides. Reformatted tables to clarify required testing frequencies. Added new table for solids, compressed gases andliquefied gases that will form peroxides. |
| 03-29-22 | Reviewed and updated links. Added information to help clarify when isopropyl alcohol must be tested. (LGS) |
| 05-16-22 | Removed section on emergency procedures (LGS) |

**References**

National Research Council (1995) Prudent Practices in the Laboratory: Handling and Disposal of Chemicals; *Evaluating hazards and assessing risks in the laboratory* (pp. 54-55). Washington, DC: The National Academies Press. https://doi.org/10.17226/4911

Bailey, J., Blair, D., Boada-Clista, L., Marsick, D., Quigley, D., Simmons, F., Whyte, H., (September/October 2004). Management of time sensitive chemicals (I): Misconceptions leading to incidents. *Chemical Health & Safety*, 14-17.

Blair, D., Boada-Clista, L., Marsick, D., Quigley, D., Simmons, F., Whyte, H., (November/December 2004). Management of time sensitive chemicals (II): Their identification, chemistry and management. *Chemical Health & Safety*, 17-24.

Quigley, D., Simmons, F., Blair, D., Boada-Clista, L., Marsick, D., Whyte, H., (January/February 2006). Management of time sensitive chemicals (I): Stabilization and treatment. *Chemical Health & Safety*, 24-29.