# University of Arizona

## Peroxide Forming Chemicals (PFC) Standard Operating Procedure

*[This is a template. Fill in all necessary blanks and delete all highlighted areas when complete. Add any sections necessary for your laboratory.]*

**Title:**  **Click here to enter the title of your SOP.**

**Approval Holder (AH):** Click here to enter text **Approval #:** Click here to enter text

**Approval Holder Phone Number(s):** Click here to enter text

**Approval Safety Coordinator (ASC):** Click here to enter text

**Approval Safety Coordinator Phone Number(s):** Click here to enter text

**Department:** Click here to enter text

1. **Purpose**

This standard operating procedure (SOP) is intended to provide guidance on how to safely store, handle, use, and dispose of peroxide forming chemicals (PFCs) in Enter AH’s name’s laboratory. Laboratory personnel should review this SOP, as well as the appropriate Safety Data Sheet(s) (SDSs), before Describe the procedure or process this SOP will address. If you have questions concerning the requirements within this SOP, contact your Approval Holder (AH) or Approval Safety Coordinator (ASC).

1. **Scope**

*[Describe when this SOP applies and to whom this SOP applies.]*

1. **Hazard Description**

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. For this reason, it is important to identify and control chemicals which 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. Refer to the tables below for some common peroxide forming chemicals and testing procedures.

Organic peroxide forming materials can form shock-sensitive organic peroxide crystals over time or upon exposure to air. **Also check each material’s SDS to determine if a chemical can form peroxides, and to check for other hazards.**

There are four classes of PFCs which have different storage requirements. Unopened containers of all four classes may be stored up to 18 months from the received date or the expiration date, whichever is sooner. Specific guidelines for allowable storage limits of opened containers based on these classifications are listed below. Extensions may be granted if the lab can demonstrate that the PFCs in question are safe to use through routine testing as described below. Labs are responsible for maintaining these testing records and if complete records cannot be produced, containers must be disposed as expired peroxide-forming hazardous waste.

**Class 1 PFCs**

Class 1 chemicals form hazardous concentrations of peroxides after prolonged storage. These must be tested monthly for peroxides starting **3 months** **from opening and disposed within 12 months of opening.**

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|  | **Class 1 PFCs** |  |
| Isopropyl ether | Potassium amide | Vinylidene chloride |
| Divinyl acetylene | Potassium metal |  |
| Divinyl ether | Sodium amide |  |

**Class 2 PFCs**

This group of chemicals will readily form hazardous concentrations of peroxides when they become concentrated (e.g., via evaporation or distillation). The concentration process defeats the action of most auto-oxidation inhibitors. As a result, these chemicals should be tested monthly for peroxides **starting 12 months from opening, or tested monthly for peroxides starting 3 months from opening if uninhibited.**

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|  | **Class 2 PFCs** |  |
| Acetaldehyde | Diethyl ether | 4-Methyl-2-pentanone |
| Cumene | 1,4-Dioxane | Tetrahydrofuran |
| Cyclohexene | Dimethoxyethane (glyme) | Tetrahydronaphthalene |
| Cyclopentene | Furan | Vinyl ethers |
| Diacetylene | Propyne |  |
| Dicyclopentadiene | Methylcyclopentane |

**Class 3 PFCs**

This group of chemicals form peroxides that can initiate polymerization. When stored neat, the likelihood of explosive polymerization due to autoacceleration dramatically increases. These chemicals should be disposed of or used within **12 months of opening, and tested monthly for peroxides starting 3 months from opening if uninhibited.**

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|  | **Class 3 PFCs** |  |
| Acrylic acid | Chlorotrifluoroethylene | Vinyl acetate |
| Acrylonitrile | Methyl methacrylate | Vinylacetylene |
| Butadiene | Styrene | 2-Vinylpyridine |
| Chlorobutadiene | Tetrafluoroethylene |  |
| Vinyl chloride (chloroethene) | 1,1-Dichloroethene |

**Class 4 PFCs**

This group of chemicals may form peroxides, but cannot clearly be defined as Class 1, 2, or 3. These chemicals should be disposed of or used within 12 months of opening, and tested monthly for peroxides starting 3 months from opening if uninhibited.

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| **Class 4 PFCs** | | |
| 1-(2-Chloroethoxy)-2-phenoxyethane | Allyl phenyl ether | Isobutyl vinyl ether |
| 1-(2-Ethoxyethoxy)ethyl acetate | å-Phenoxypropionyl chloride | Isophorone |
| 1,1,2,3-Tetrachloro-1,3butadiene | Benzyl 1-naphthyl ether | Isopropyl2,4,5trichlorophenoxyacetate |
| 1,1-Dimethoxyethane | Benzyl ether | Limonene |
| 1,2-Bis(2-  chloroethoxy)ethane | Benzyl ethyl ether | m,o,p-Diethoxybenzene |
| 1,2-Dibenzyloxyethane | Benzyl methyl ether | Methoxy-1,3,5,7cyclooctatetraene |
| 1,2-Dichloroethyl ethyl ether | Benzyl n-butyl ether | Methyl p-(namyloxy)benzoate |
| 1,2-Diethoxyethane | Bis(2-(methoxyethoxy)ethyl) ether | m-Nitrophenetole |
| 1,2-Epoxy-3- | Bis(2-chloroethyl) ether | n-Amyl ether |

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| isopropoxypropane |  |  |
| 1,2-Epoxy-3-phenoxypropane | Bis(2-ethoxyethyl) adipate | n-Butyl phenyl ether |
| 1,3,3-Trimethoxypropene | Bis(2-ethoxyethyl) ether | n-Butyl vinyl ether |
| 1,3-Butadiyne | Bis(2-ethoxyethyl) phthalate | n-Hexyl ether |
| 1,3-Dioxepane | Bis(2-methoxyethyl) carbonate | n-Methylphenetole |
| 1,5-p-Methadiene | Bis(2-methoxyethyl) ether | n-Propyl isopropyl ether |
| 1-Ethoxy-2-propyne | Bis(2-methoxyethyl)phthalate | n-Propylether |
| 1-Ethoxynaphthalene | Bis(2-methoxymethyl) adipate | o,p-Ethoxyphenyl isocyanate |
| 1-Octene | Bis(2-n-butoxyethyl) phthalate | o,p-Iodophenetole |
| 1-Pentene | Bis(2-phenoxyethyl) ether | o-Bromophenetole |
| 2,2-Diethoxypropane | Bis(4-chlorobutyl) ether | o-Chlorophenetole |
| 2,4-Dichlorophenetole | Bis(chloromethyl) ether | Oxybis(2-ethyl acetate) |
| 2,4-Dinitrophenetole | Buten-3-yne | Oxybis(2-ethyl benzoate) |
| 2,5-Hexadiyn-1-ol | Chloroacetaldehyde diethylacetal | p-(n-Amyloxy)benzoyl chloride |
| 2-Bromomethyl ethyl ether | Chloroethylene | p-Bromophenetole |
| 2-Chlorobutadiene | Chloromethyl methyl ether | p-Chlorophenetole |
| 2-Ethoxyethyl acetate | Cyclooctene | p-Dibenzyloxybenzene |
| 2-Ethoxyethyl)-o-benzoyl benzoate | Cyclopropyl methyl ether | p-Di-n-butoxybenzene |
| 2-Ethylacrylaldehyde oxime | Di(1-propynyl) ether | Phenoxyacetyl chloride |
| 2-Ethylbutanol | Di(2-propynyl) ether | Phenyl o-propyl ether |
| 2-Ethylhexanal | Diallyl ether | p-Isopropoxypropionitrile |
| 2-Methoxyethanol | Diethoxymethane | p-Phenylphenetone |
| 2-Methoxyethyl vinyl ether | Diethyl acetal | Sodium 8,11,14eicosatetraenoate |
| 2-Methyltetrahydrofuran | Diethyl  ethoxymethylenemalonate | Sodium ethoxyacetylide |
| 3,3-Dimethoxypropene | Diethyl fumarate | ß,ß-Oxydipropionitrile |
| 3-Bromopropyl phenyl ether | Diethylketene | ß-Bromophenetole |
| 3-Ethoxyopropionitrile | Dimethoxymethane | ß-Chlorophenetole |
| 3-Methoxy-1-butyl acetate | Dimethylketene | ß-Methoxypropionitrile |
| 3-Methoxyethyl acetate | Di-n-propoxymethane | tert-Butyl ethyl ether |
| 4,5-Hexadien-2-yn-1-ol | Ethoxyacetophenone | tert-Butyl methyl ether |
| 4-Methyl-2-pentanone | Ethyl ß-ethoxypropionate | Tetrahydropyran |
| 4-Vinyl cyclohexene | Ethyl vinyl ether | Triethylene glycol diacetate |
| Acrolein | Furan | Triethylene glycol dipropionate |
| Allyl ether | Isoamyl benzyl ether | Vinylenecarbonate |
| Allyl ethyl ether | Isoamyl ether | Vinylidene chioride |

1. **Hazard Controls**

*[Describe how to safely set up the procedure or process.]*

* 1. **Engineering Controls**

Use 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.

* 1. **Work Practice Controls**
* PFCs should be stored in airtight containers in a dark, cool, and dry place.
* PFC containers should be labeled with the **date received and the date opened**.
* Store the PFC container with the chemical label and dates facing forward to minimize container handling.
* Maintain the smallest amount necessary for ongoing work.
* 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.**
* 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.
* 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
* Note: Never try to force open a rusted or stuck cap on a container of a peroxide-forming chemical.
  1. **Personal Protective Equipment**

*[Describe the personal protective equipment needed to adequately protect laboratory workers when performing the process or procedure addressed by this SOP. Ensure to specify any personal protective equipment beyond the minimum (i.e. safety glasses, lab coat, gloves, long pants and closed-toed shoes).]*

Wear standard nitrile laboratory gloves (or those recommended on the SDS), lab coat, and safety glasses (meeting the requirements of ANSI/ISEA Z87.1) for all work in the laboratory. Contact RLSS if additional PPE is required or there are questions/uncertainty about the requisite PPE.

* **Hand and Arm Protection**: Elbow-length, acid resistant gloves should always be used when creating, working with, or cleaning up aqua regia solutions.
* **Face and Eye Protection**: Safety goggles are a minimum protection; the use of a face shield with eye protection is strongly recommended to protect both the eyes and face from splashes.
* **Body Protection**: A 100% cotton lab coat should be used; flame resistant coats can also be used.
  1. **Transportation and Storage**
* Store in airtight containers in a dark, cool but not freezing, and dry 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 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.

1. **Process**

*[Describe the steps needed to complete this procedure or process in a safe manner. Use as much detail as is necessary to ensure all laboratory workers can complete the procedure or experiment safely.]*

**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 (as indicated in Table 2) for a particular peroxide forming chemical, the person using the chemical should either dispose of it or test it for peroxide content. Any container found to have a peroxide concentration greater than or equal to 100 PPM should be disposed of (call EH&S at 509-963-2338 for assistance).

Materials which are older than the suggested shelf life but have been tested and have no detectable peroxides or **peroxide concentrations <100 PPM may be retained but should be tested at frequent intervals** (see Table 2). *All chemicals which are to be distilled must be tested prior to distillation regardless of age.* **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.

RLSS strongly recommends the **use of peroxide test strips** to determine the presence of peroxides in PFCs. These are the most convenient method and are available through Sigma Aldrich/Millipore Sigma and several other suppliers. These strips are simple to use: a strip is immersed in the chemical, exhaled upon to initiate a color change, which is then assessed against a scale to determine the concentration.

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However, other testing methods are available; please contact RLSS for alternative methods and information at RLSS-help@arizona.edu.

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| **Table 2: Safe storage period for peroxidizable chemicals** | |
| **Peroxidizable Chemical Classification** | **Dispose or Test After:1** |
| Unopened chemicals from the manufacturer | 12 months |
| Opened containers |  |
| List A, Table 1 materials | 3 months |
| List B, Table 1 materials | 12 months |
| Uninhibited List C, Table 1 materials | 24 hours |
| Inhibited List C, Table 1 materials | 12 months2 |

1 Never open or test containers of unknown origin or age or that have visible evidence of peroxides

2 Do not store under inert atmosphere.

1. **Cleanup & Disposal**

*[Describe how to safely end the procedure or process, clean up the process, and dispose of any waste generated.]*

**Do not handle** the container if, when in the laboratory, you come across PFCs:

* That are >2 years past the list expiration date **OR** if there is no date listed;
* Wherevisiblecrystallization is present:
  + Interior: typically appears as white floating particles.
  + Exterior: powdery white material on the cap, in the cap threads, or forming a large “cauliflower” like abscess.

In either event, **secure the area** where the container is stored to prevent anyone from accessing it and contact Risk Management Services (520-621-1790) **immediately** for pick-up and disposal.

1. **Enter Additional Section Title**

*[Add as many sections as necessary to adequately describe how to safely perform the procedure or process addressed by this SOP.]*

**8. References**

* <http://www.ilpi.com/msds/ref/peroxide.html><https://e-reports-ext.llnl.gov/pdf/235232.pdf>
* <http://ccehss.berkeley.edu/sites/default/files/pdf/section7_insert17.pdf>