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HEALTHY AND SAFE LABS 24/7

Peroxide-Forming Chemicals Procedures

June 1, 2023

BACKGROUND

Peroxides (chemicals containing an R-O-O-R structure) can be quite reactive as the oxygen-oxygen bond is relatively unstable and can often be broken with just a small energy input such as heat or shock. Peroxides can be inadvertently formed in a variety of organic and inorganic compounds and have resulted in explosions and injuries to researchers and support staff in academic settings [1-4].

These peroxide-forming chemical (PFC) procedures outline Western Washington University's requirements for managing PFCs and details Environmental Health and Safety's (EHS's) procedures for assessing peroxide risk and handling unwanted and waste solutions.

All groups handling peroxide-forming chemicals are responsible for the regular testing, stabilization, and disposition of such chemicals. In addition, any groups handling peroxide forming chemicals must develop a Standard Operating Procedure for their use.

CLASSIFICATION

Universities classify PFCs in a variety of ways [5-7]. Western Washington University utilizes the frequently used 4-class categories:

- Class A – Severe Peroxide Hazard – May spontaneously decompose and explode even without substantial concentration.
- Class B – Concentration Hazard – Forms explosive peroxides when evaporated, distilled, or concentrated. Requires external energy to decompose/explode.
- Class C – Shock and Heat Sensitive – May undergo hazardous polymerization in the presence of peroxides.
- Class D – Potential Peroxide Forming Chemicals – May form peroxides but generally do not accumulate to hazardous levels.

These different categorizations have different retention and testing schedules associated with them.

The table below lists some of the most commonly used chemicals within each category. The University of Minnesota (UMN) maintains a database of nearly 250 chemicals that are known or suspected PFCs along with hazard classifications.

The UMN database has been entered into Chimera so that groups can run a Customized Group List Report for "Peroxide-Forming Chemicals". It is important to note that there are more peroxidizable chemicals than are found in these sources. If you suspect a chemical is a peroxide former but is not found in these lists, please contact EHS.

Table 1: Peroxide-Forming Chemical Classes Observe ALL Expiration Dates Listed on the Container			
Class A Discard within 3 months after opening in air or test for peroxides before heating, distillation, or disposal. Evaluation/testing is required every 6 months after opening in air.	Class B Discard within 6 months after opening in air or test for peroxides before heating, distillation, or disposal. Evaluation/testing is required every 12 months after opening in air.	Class C Discard within 6 months after opening in air or test for peroxides before heating, distillation, or disposal. Evaluation/testing is required every 12 months after opening in air.	Class D Discard within 12 months after opening in air or test for peroxides before heating, distillation, or disposal. Evaluation/testing is required every 24 months after opening in air.
Divinyl ether Isopropyl ether Potassium amide Potassium metal Vinylidene chloride	Tetrahydrofuran (THF) Diethyl ether 1,4-dioxane Benzyl alcohol Methyl cyclopentane 2-propanol (isopropanol) 2-pentanol	Styrene Methyl methacrylate Acrylic acid Acrylonitrile Vinyl acetate	Benzaldehyde 1-pentene Isoamyl ether Benzyl ether

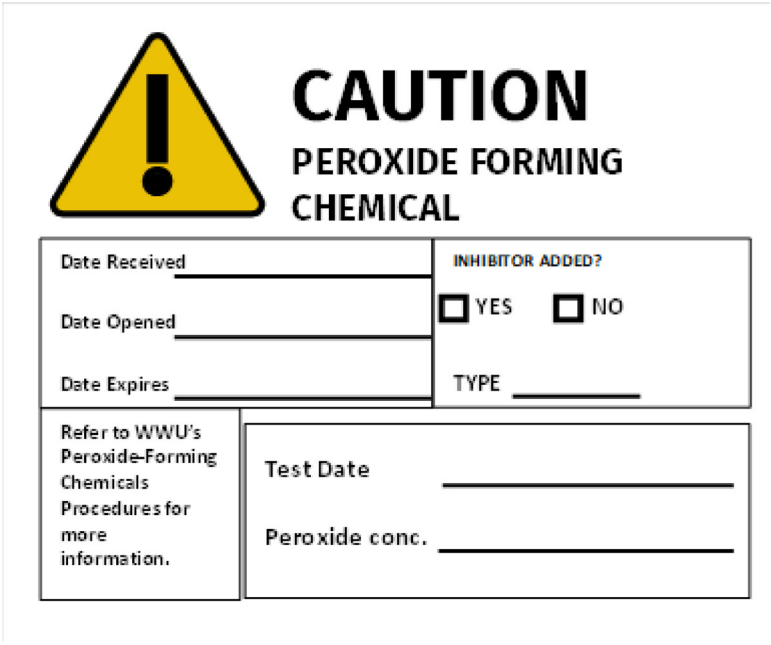
STORAGE and USE

In general, PFCs should be stored in amber bottles or metal cans away from sources of light and heat. Containers should remain tightly sealed when in storage.

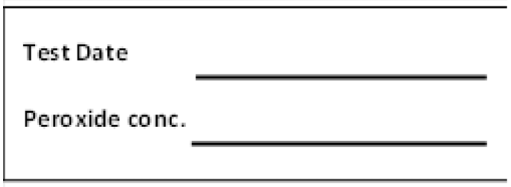
Chemicals should be stabilized with an appropriate antioxidant, or if the chemical needs to be handled without stabilizers, it is best to store under an inert atmosphere.

Many PFCs can be stabilized with antioxidants that scavenge free oxygen radicals and prevent the formation of additional peroxides. Add 1 gram of butylated hydroxytoluene (BHT) or other suitable antioxidant per liter of chemical. It is important to recognize that this process only slows/prevents additional formation of peroxides and does not destroy or deactivate peroxides.

Maintain an up-to-date inventory of all chemicals in CHIMERA. Users can perform checks of their own PFC inventory and EHS can screen the campus inventory for most common PFCs and follow up with groups to ensure that chemicals are being stored, handled, and disposed of properly. Refer to Appendix A for instructions on how to run a PFC inventory report in CHIMERA.



All PFC containers must be labelled with a peroxide forming chemical label (shown to the right on an AVERY 5164 label). Additional 'Test Date and Peroxide Concentration' info can be added by overlaying stickers (shown to the right on an AVERY 5160 label). If a chemical has an expiration date supplied by the manufacturer, that expiration date must be observed. Otherwise, testing schedules must be set by the chemical owner based on the chemical's classification. You may also email EHS for stickers as needed. For smaller bottles/containers, consider placing a wire or ribbon shipping tag around the bottle cap or place the container in a bag and label the bag with the sticker.



EVALUATION, TESTING, and DISPOSAL

It is the responsibility of the chemical owner to perform regular testing of their own PFCs. Faculty may train qualified employees and students to perform peroxide evaluation and testing. Lawrence Berkeley National Laboratory (LBNL) has created a helpful training video that may be used in training, but note that certain references may be specific to LBNL's procedures. Safety training must be documented for personnel carrying out these procedures. For chemicals that are shared use, such as stockroom/academic use chemicals, it is the Department Safety Coordinator or stockroom manager's responsibility to perform regular testing of those chemicals.

EHS will not collect PFCs for disposal that have exceeded their retention times (Table 1) unless the peroxide concentration is below 10mg/L and stabilized. While EHS recognizes that this limit is conservative from a safety standpoint, our hazardous waste vendor will only transport peroxide forming chemicals that have been stabilized and have peroxide concentrations at or below 10mg/L.

- PFCs that are within the retention times in Table 1 can be scheduled for pickup using the normal hazardous waste processes without stabilization or testing requirements.
- Any material that contains PFCs in Class B, C, or D ≥ 50% by volume and has exceeded the retention time of the PFC must be tested for peroxides prior to disposal.
- Any material that contains PFCs in Class A ≥ 10% by volume and has exceeded the retention time of the PFC must be tested for peroxides prior to disposal.

For each peroxide-forming chemicals that has exceeded the retention times listed in Table 1, follow the steps below before requesting a hazardous waste pick-up:

1. **Determine the age of the chemical.** If chemicals are beyond the ages listed below, contact EHS for evaluation (360-650-3064) before moving onto step 2.
    a. For Class D chemicals, you may move onto step 2 if the container is <2 years old and opened or <3 years old and unopened.
    b. For Class B and C chemicals, you may move onto step 2 if the container is <1 year old and opened or <2 years old and unopened.
    c. For Class A chemicals, you may move onto step 2 if the container is <6 months old and opened or <1 year old and unopened.
2. **Visually inspect the chemical container.** If any visual signs of peroxides are present, immediately contact EHS (360-650-3064). Do not handle the chemical any further. Ensure that others do not handle the chemical by barricading and/or signing the area off. Do not move onto step 3.
    a. Signs of significant peroxide formation include: wispy/needle-like crystals, viscous liquid layers, and cloudiness. If these are observed, cease chemical handling.
    b. If the volume of the container has evaporated to less than 10% of the original volume, consult with EHS before moving on.
3. **Test for peroxides.**
    a. Test strips are suitable for the testing of simple ethers such as diethyl ether, tetrahydrofuran, and p-dioxane. Always refer to the manufacturer's instructions for proper use and interpretation of these test strip results. EHS recommends the use of Supelco, MQuant Peroxide Test Strips, 1-100mg/L, 110081 or other similar test.
    b. The iodine test can be used for any peroxide-forming chemical.
        i. Dissolve 100mg potassium iodide in 1mL glacial acetic acid.
        ii. In a small beaker or cylinder, add the potassium iodide solution to 1mL of the peroxide forming chemical.
        iii. Determine the color of the mixture by placing against a white sheet of paper behind the beaker/cylinder.
            1. A pale or barely discernable yellow color indicates peroxide concentration of 10 – 50 mg/L
            2. A bright yellow or brown color indicates peroxide concentration in excess of 50mg/L.
4. **Stabilize the chemical.**
    a. If peroxide concentrations are ≤ 10mg/L, solutions can continue to be used. If disposing of the chemical, stabilize the chemical, making note of the date it was added and the peroxide concentration. The solution can then be scheduled for pickup using the normal hazardous waste processes.
    b. If peroxide concentrations are > 10mg/L but ≤ 100mg/L, solutions can continue to be used but **should not be distilled or evaporated**. You must go on to step 5 before scheduling these solutions for pickup.
    c. If peroxide concentrations are > 100mg/L, solutions should not be used. You must go on to step 5 before scheduling these solutions for pickup.
5. **Removal/Destruction of Peroxides.**
    a. Lab personnel may remove and/or destroy peroxides if they are trained and comfortable in doing so. One particular method to remove peroxides from solution involves filtering the solution through basic alumina. It is important to recognize that not all peroxides decompose when passed through the alumina and may be dangerous if dried. Additionally, filtration through alumina may also remove inhibitors from the PFC solution. Another method for the controlled destruction of peroxides involves mixing the PFC solution with a ferrous sulfate solution. SOPs must

be made for any destruction methods and personnel must receive safety training. Please reach out to EHS for suitable methods based on PFCs you handle.

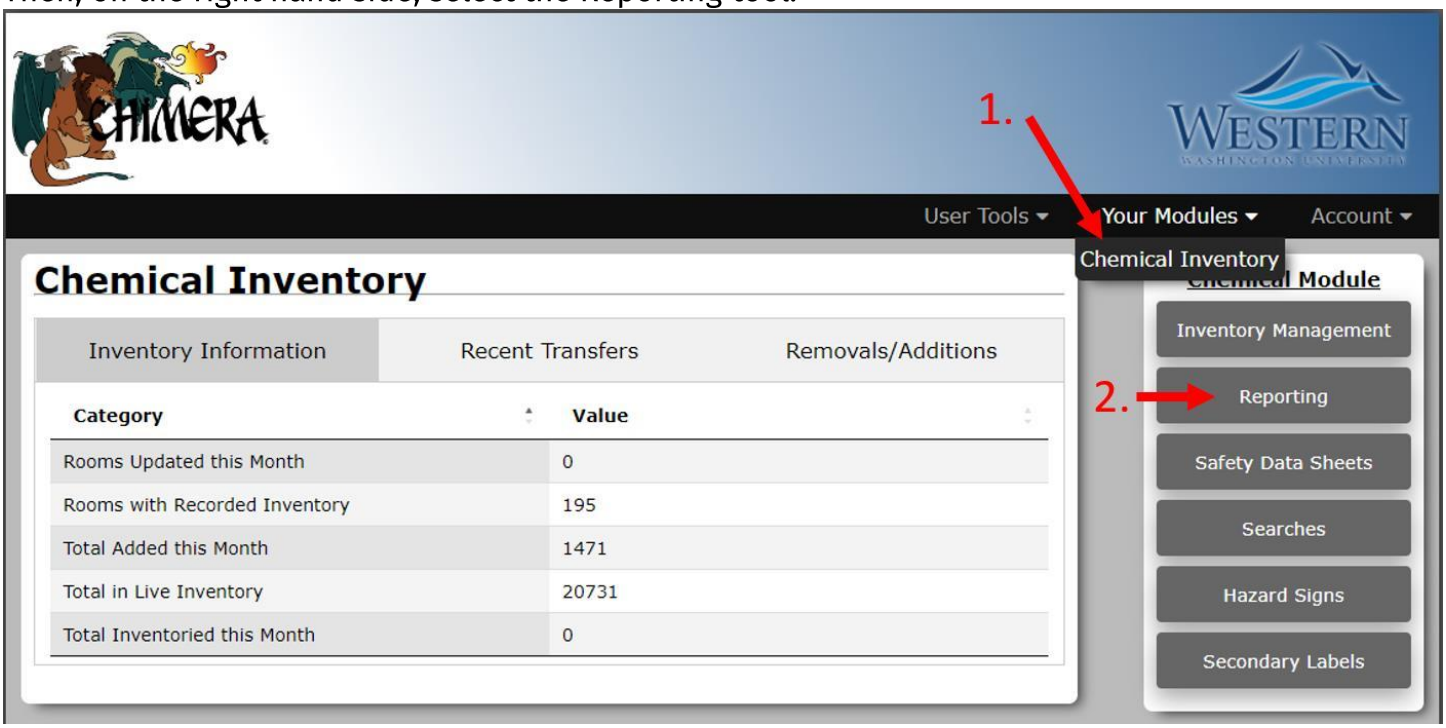
b. If lab personnel are not comfortable in deactivating peroxides, contact EHS. Any solutions that EHS personnel do not feel comfortable treating may need to be handled by a specialist hazardous materials contractor.
c. After peroxide destruction, solutions should be stabilized. They can then be scheduled for pickup using the normal hazardous waste processes.

REFERENCES

1. CRC Handbook of Laboratory Safety, 5th Edition, Chapter 4, D. Ethers. A. Keith Furr
2. Berkley Office of Environment, Health & Safety: Peroxide Explosion Injures Campus Researcher
3. University of Minnesota, University Health & Safety: Dangers of Peroxide Formers – Explosion at UMN
4. Chemical & Engineering News: Chemical safety: peroxide formation in 2-propanol
5. University of Washington EH&S Guidelines for Peroxide Forming Chemicals
6. Weill Cornell Medicine EHS Peroxide-Forming Chemicals
7. University of California Santa Cruz Environmental Health & Safety Peroxide Forming Chemicals
8. Lawrence Berkeley National Laboratory: Testing Peroxide-forming Chemicals Training Video

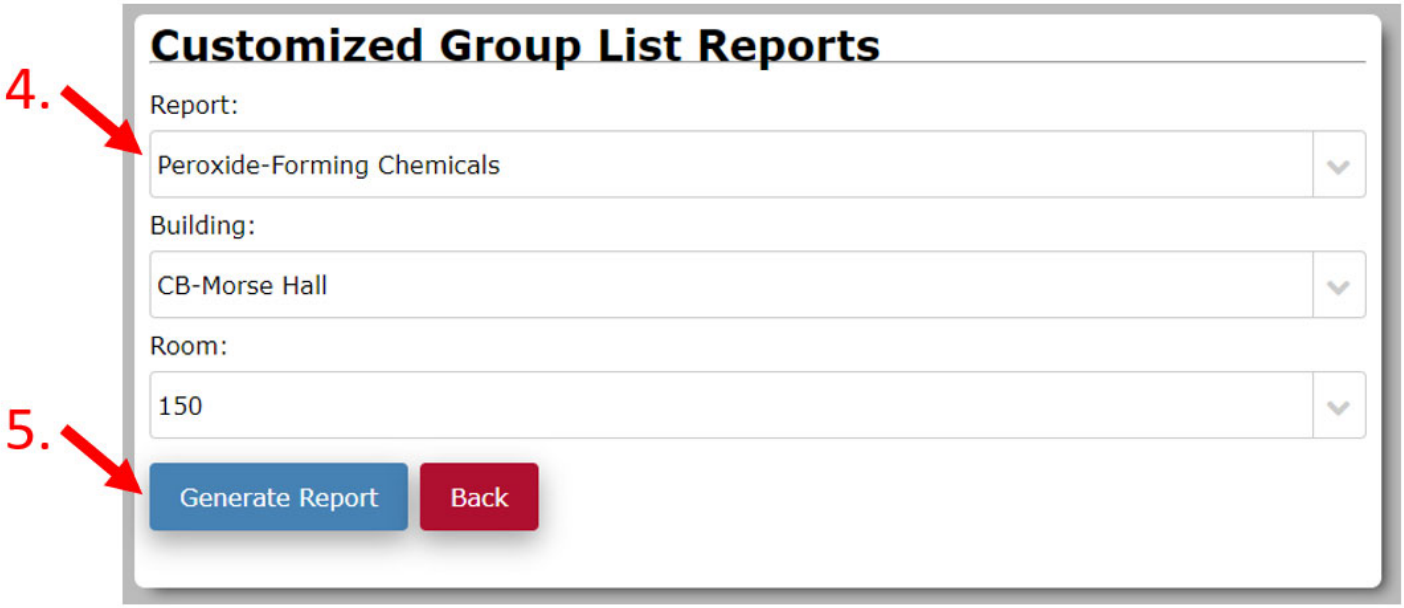
APPENDIX A
Searching CHIMERA for PFCs

Upon logging into CHIMERA, access the Chemical Inventory Module.
Then, on the right hand side, select the Reporting tool.



From the Reports page, select Customized Group List Reports.

Then, you will select the Peroxide-Forming Chemicals Report and the Building and Room that you want to run the report on. You are then ready to run the report and can select Generate Report.



The report will list PFCs in order of Group letter (from A to D). It will also include the barcode associated with each item, the Location within the room if provided by the user, the product name, the PFC component name, the CAS, the percentage of PFC in the product, any comments provided by the user, the amount/units, and the expiration date if provided by the user.