1. Purpose

This standard operating procedure (SOP) establishes procedures for the safe handling, transportation, use and storage of peroxide forming chemicals (PFCs).

2. Hazard Identification

PFCs have unique properties of forming explosive peroxide (containing -O-O- bond to form organic peroxide) and shock sensitive crystals via "auto-oxidizing" with atmospheric oxygen under ambient conditions. Some of these compounds build up rapidly to potentially dangerous levels creating a hazard to lab personnel depending on solvent impurities, exposure to air, and/or auto-polymerization. Most manufacturers add inhibitors or stabilizers, which retard peroxide formation, extend storage life of the product, and make the chemical less sensitive to mechanical or thermal shock. However, heating, mishandling, or distilling these chemicals may remove these stabilizers thereby concentrating the peroxides, creating a higher risk of violent explosions. Additionally, a second potentially dangerous situation may occur when lab personal allow these peroxide forming chemicals to evaporate to dryness when exposed to air (e.g., leaving the cap off a bottle for extended periods of time), creating explosive and shock sensitive crystals on the sides and bottom of the bottle. PFCs are considered a particularly hazardous substance (PHS) due to flammability, volatility, and potential to form explosive peroxides over time. For more information, consult the safety data sheet (SDS). As well as other sources of information such as the National Academic Press' Safety Summary on Peroxide Formers.

3. Scope

This SOP addresses only the general use of peroxide forming chemicals and its solutions in the laboratory. Refer to the SDS for specific safety hazards and handling precautions. The SOP applies to all Kennesaw State University (KSU) employees, students, and contractors. It assumes that all KSU minimum safety requirements, as detailed in the KSU Chemical Hygiene and Safety Plan (EOSMS-201) have been implemented.

4. Personnel Qualifications

All faculty, staff, and students using or handling a PFC within a laboratory are responsible for understanding all hazards associated with PFCs and for following appropriate safety protocols, including completing required training and using appropriate personal protective equipment (PPE). Use of PFCs is restricted to specific employees or students with prior training in proper use, handling,, storage, and emergency procedures of the PFC.

5. Principal Investigator and Laboratory Personnel Responsibilities

The principal investigator (PI) or laboratory supervisor/coordinator/manager is responsible for ensuring that staff and students under their supervision have been trained in using, storing, and handling PFCs and all associated emergency procedures. PIs and laboratory personnel will provide guidance in assessing hazards, establishing engineering and administrative controls and good work practices, and selecting PPE. Records of this training must be retained by the department and a copy must be forwarded to the Environmental Health and Safety (EHS) Department. EHS will perform and document exposure monitoring to determine employee exposures to hazardous materials and to evaluate the adequacy of controls.

6. Health and Safety Hazards of Peroxide Forming Chemicals

PFCs have specific permissible exposure limits (PELs) which cannot be exceeded. Since this is a highly volatile chemical, inhalation exposure is a major concern. Exposure at high concentrations can cause sedation, unconsciousness, and respiratory paralysis. PFCs are sufficiently volatile and may produce a peroxide hazard if exposed to atmospheric oxygen for prolonged periods, creating an explosion/fire risk.

PFCs may be classified as one of three categories based on the potential to form peroxides and the associated hazards (i.e., Class A, Class B, and Class C). See **Appendix B** for a list of many commonly known peroxide formers and their associated categories. Some of these are commonly used in organic chemistry laboratories (e.g., diethyl ether, tetrahydrofuran, isopropanol, dicyclopentadiene, and cyclohexene) can form peroxides if not properly handled, used, or stored. However, this list in Appendix B is not all-inclusive; therefore, please consult with the manufacturer's SDS for additional guidance or contact EHS Department at 470-578-3321 or ehs@kennesaw.edu.

7. Requirement for Working with Peroxide Forming Chemicals

A. Hazard and Risk Assessments

The PI or laboratory supervisor/coordinator/manager must be aware of and approve the work performed under their jurisdiction and shall ensure that an appropriate hazard assessment for the use of peroxide forming chemicals has been conducted. EHS may be consulted to provide assistance in performing hazard assessments.

Each new operation using PFCs must be evaluated individually; assessment of the level of risk depends on how the substance will be used. The assessment should ensure appropriate protective measures have been put into place and that the proper level of work authorization has been obtained before commencing the operation.

B. Hazard Prevention and Control

The hazards of PFCs can be mitigated by a variety of means including chemical substitution, engineering controls, administrative controls, PPE, and work practices. The general control measures are discussed in this section. The PI or laboratory supervisor/coordinator/manager must develop control measures specific to the particular operation after conducting the appropriate hazards assessment and develop a separate SOP specific to the operation/project.

1. Chemical substitution

Before peroxide forming chemicals are selected for use in a particular operation/process, a safer alternative chemical should be considered for use in lieu of organic peroxides.

2. Engineering Controls

Because of its high volatility and the possibility of aerosol formation, PFCs must be handled in a chemical fume hood under negative pressure. The chemical fume hood must have been certified within the last 12 months and must function within the acceptable flow rate range. Work should be performed with the sash lowered as much as possible.

3. Work Practice Controls

Gloves, lab coat, and safety glasses must be worn when working with PFCs.

Wearing nitrile gloves should provide adequate hand protection for use of these chemicals. Change gloves regularly (at least every two hours) or when they obtain a breach. Wash your hands when changing gloves.

If splashes may occur, wear safety goggles and a face shield instead of safety glasses. Safety glasses do not provide adequate protection from splashes.

Use a less dangerous product than PFCs, if possible, or purchase in dilute solutions.

Always transfer the chemical from one container to another inside of a fume hood. When transferring the chemical from one container to another, only pour the amount that is needed. Ensure proper grounding and avoid creating static electricity by grounding metal containers when transferring flammable liquids.

Keep away from ignition sources such as open flames, hot surfaces, steam baths, heat guns, and sparking devices. **Eliminate ignition sources such as open flames, hot surfaces, heat guns, steam baths, and operation of mechanical and electrical equipment that is not intrinsically safe**.

Consider the following:

- Distillations and evaporation could create unsafe conditions if PFCs are allowed to concentrate. **PFCs may concentrate during distillation or evaporation experiments, which may lead to a shock sensitive explosion, especially if the chemicals are allowed to evaporate to dryness**.
- Low temperature work could cause peroxides to fall or “crash” out of solution as they near the freezing point depression.
- Using liquid column chromatography could cause peroxides to accumulate at the top of the column depending on if it dries out and becomes exposed to atmospheric oxygen.

<u>DO NOT</u> attempt to open a visibly dented, rusty, bulging, or otherwise compromised container of a peroxide forming chemical. Contact EHS if this occurs.

When possible, purchase PFCs with peroxide forming inhibitors or stabilizers.

Purchase diethyl ether in metal (e.g., aluminum) containers, which aid in peroxide formation prevention. Keep all containers of peroxide forming chemicals closed as much as possible. These are highly volatile chemicals and open containers will result in inadvertent release of flammable vapors. **It is recommended that containers of PFCs not be kept longer than one year or past the expiration date listed by the manufacture on the bottle. Ensure that containers are dated upon receipt and at the time they are opened. If tested, note the date it was tested**.

C. Handling, Testing, and Storage

PFCs are incompatible with strong oxidizers, strong acids, and halogens. To avoid violent reactions, store them away from these chemicals in an appropriate flammables cabinet. Ensure that the containers are stored away from light and purge the headspace of the bottle with inert gas, such as nitrogen, which displaces air from with inside, to prolong shelf life of the chemical and to help prevent peroxide formation.

PFCs without inhibitors **SHOULD** be stored under inert gas, whereas some PFCs with inhibitors should **NOT** be stored under inert gas because the inhibitors or stabilizers **REQUIRE** oxygen to prevent peroxides formation.

Periodically test PFCs containers for peroxides formation with commercially available peroxide test strips. Consult with EHS for guidance for proper testing procedures. Refer to the "Health and Safety Hazards of Peroxide Forming Chemicals" section of this document for information on the different classes of PFCs. Below are suggested safe storage and testing protocols for peroxide forming chemicals:

- **Class A**: Test for peroxides before using and discard the bottle 3 months after opening. Discard unopened bottles before manufacturer's expiration date, usually up to 18 months.
- **Class B**: Test for peroxides before distillation or evaporation experiments and discard the bottle 12 months after opening. Discard unopened bottles before manufacturer's expiration date, usually up to 18 months.
- **Class C**: If no inhibitors or stabilizers are present, discard bottle 24 hours after opening. If inhibitors or stabilizers are used, test for peroxides within 12 months after opening the bottle. Discard unopened bottles before manufacturer's expiration date, usually up to 18 months.

Labeling should include:

- Date received
- Date opened
- Expiration Date from manufacturer
- Peroxide test date (once open) along with any results

Once work is complete, wipe down the work area with a soap and water solution.

D. Emergency Procedures

In the event of an emergency involving peroxide forming chemicals, contact the KSU Police Department by dialing extension 6666 or 470-578-6666.

Since these chemicals are highly flammable, be aware of the location of the nearest fire extinguisher.

Be prepared to communicate what the emergency is, how many people are involved and what is the extent of their injuries or illnesses. Remove the person to fresh air. Evacuate adjoining laboratories, as necessary. Notify the PI or laboratory supervisor/coordinator/manager. Report the incident to EHS as soon as possible and complete an incident report through the Reliance system.

Emergency Contact

ex. 6666

1. Accidental Exposure to Peroxide Forming Chemicals

Refer to the SDS of the chemical for exact procedures. In general, if peroxide forming chemical vapor has been inhaled, move the victim to fresh air immediately. If spilled on the skin or clothing, wash the affected area with large amounts of soap and water, using a safety shower or eyewash, as appropriate, for a minimum of 15 minutes. During washing, remove contaminated clothing and footwear. Remove goggles last. Those assisting the victim should wear appropriate PPE including protective gloves. A disposable laboratory coat, scrubs, or jumpsuit should be available for the exposed individual to wear after using a safety shower.

If exposure to the eyes has occurred, immediately flush affected eye(s) for at least 15 minutes without stopping. Hold upper and lower eyelids open and away from the eyes during irrigation. Do not allow victim to rub eyes or keep eyes closed. Remove contact lenses if possible. (Note: contact lenses should not be worn when working with this material.) If necessary, continue flushing with personal eyewash or apply ice water compresses during transport to a medical facility or eye specialist. **Seek medical attention immediately.**

If PFCs are ingested, do not induce vomiting, but flush mouth immediately. Never give anything by mouth to an unconscious person. **Seek medical attention immediately.**

PFCs exposure requires immediate first aid and medical treatment. Prompt first aid is essential, even if the victim does not exhibit any signs or symptoms, or feel any pain. After seeking medical attention, contact EHS Department to report the accident or incident.

2. Spill Clean-up

Spill clean-up must be performed by properly trained individuals. Do not attempt to clean up a spill of pure peroxide forming chemical or a solution of greater than 5% unless you have been properly trained.

Wipe up solutions with chemical absorbent pads. Once the spill has been completely absorbed, wipe the area down at least twice using a soap and water solution.

Waste generated from a spill must be handled as hazardous waste.

E. Waste Management

Contact EHS for waste disposal procedures for PFCs.

8. Training Requirements

All faculty/staff/students who work with PFCs are required to complete the OwlTrain online training course “Laboratory Safety” and the course “Globally Harmonized System of Classification and Labeling of Chemicals (GHS)”.

They are also required to read and fully comply with this SOP for peroxide forming chemicals. Use the form in **Appendix A** below to record training for this SOP.

Appendix A: SOP Review Record Form for Peroxide Forming Chemicals

To be completed by the employee/student

Peroxide forming chemicals (PFCs) are considered a particularly hazardous substance (PHS) due to its flammability, volatility, and potential to form explosive peroxides. To manage risks associated with use of peroxide forming chemicals and to ensure the safety of KSU employees and students, the University has established a standard operating procedure (SOP) for the safe handling of PFCs.

The procedure requires that all faculty/staff/students who work with peroxide forming chemicals complete the appropriate safety training and read and comply with the SOP for PFCs. This form, therefore, should be completed and signed by each KSU employee or student who works, or plans to work with PFCs, as documentation that the individual has read and understood the requirements of the SOP.

Name			☐ Faculty ☐ Staff ☐ Student
Job Title		Department	
Supervisor's Name			
By signing this form, I certify that I have read, understood, and will comply with the requirements of this SOP for safe handling of Peroxide Forming Chemicals.			
Signature		Date	
Note:			

Appendix B: List of Commonly Known Peroxide Formers

Class A: Chemicals in this class may produce a severe peroxide hazard if exposed to air/oxygen for prolonged periods, creating a high explosion risk **without concentration**.

Isopropyl ether	Butadiene	Sodium amide
Chlorobutadiene (Chloroprene)	Potassium metal	Tetrafluoroethylene
Vinylidine chloride	Potassium amide	Divinyl acetylene
Tetrahydrofuran (without inhibitor)		

Class B: Chemicals in this class are sufficiently volatile and may produce a peroxide hazard if exposed to atmospheric oxygen for prolonged periods, creating an explosion risk **upon concentration during distillation or evaporation**.

Acetal	Diethylene glycol dimethyl ether	Methyl-isobutyl ketone
Acetaldehyde	Diethyl ether	4-Methyl-2-pentanol
Benzyl alcohol	Dioxane	2-Pentanol
2-Butanol	Furan	4-Penten-1-ol
Chlorofluoroethylene	4-Heptanol	1-Phenylethanol
Cyclohexene	2-Hexanol	Tetrahydrofuran
2-Cyclohexene-1-ol	Methyl acetylene	Vinyl ethers
Cyclopentene	3-Methyl-1-Butanol	Isopropanol
Dicyclopentadiene	Methyl cyclopentane	

Class C: Chemicals, unsaturated monomers, in this class may form explosive levels of peroxides by autopolymerize if inhibitors are depleted or not present during prolonged storage conditions.

Acrylic acid	Methyl methacrylate	Vinyl chloride
Butadiene	Styrene	Vinyl pyridine
Chlorotrifluoroethylene	Tetrafluoroethylene	
Ethyl acrylate	Vinyl acetate	