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	Peroxide Forming Chemicals		
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1.0 PURPOSE:

Materials that are susceptible to peroxide formation (i.e., autooxidation) are ones that typically react with air, moisture or impurities and produce a change in their chemical composition in normal storage. The peroxides that form are less volatile than the solvent itself and thus tend to concentrate. This is particularly dangerous if peroxides are present during a distillation, where the applied heat to the concentrated solution may trigger a violent explosion. Equally dangerous is to allow a container of this material to evaporate to dryness, leaving the crystals of peroxide at the bottom of the container.

2.0 SCOPE:

This procedure applies to all Louisiana State University Personnel that use and store peroxide forming chemicals. This standard operating procedure (SOP) is intended to provide general guidance on how to safely and store peroxide formers. This SOP is generic in nature and only addresses safety issues pertaining to stability hazards of chemicals. If you have questions concerning the applicability of any item contact the Principal Investigator/Laboratory Supervisor of your laboratory or Environmental Health and Safety.

3.0 **RESPONSIBILITIES**:

Only trained and qualified personnel shall be allowed to work with peroxide forming chemicals. Supervisors are responsible for ensuring that personnel are trained to in the safe use of reactive chemicals.

4.0 **DEFINITIONS**:

4.1 Organic peroxides are among the most hazardous substances used in the laboratory - both fuels and oxidizers in one. They are typically low power explosives and very easy to initiate through sparks or shocks. Materials that are susceptible to peroxide formation (i.e., autoxidation) are ones that typically react with air, moisture or impurities and produce a change in their chemical composition in normal storage. The peroxides that form are less volatile than the solvent itself and thus tend to concentrate. This is particularly dangerous if peroxides are present during a distillation, where the applied heat to the concentrated solution may trigger a violent explosion. Equally dangerous is to allow a container of this material to evaporate to dryness, leaving the crystals of peroxide at the bottom of the container. Some materials, such as ethers, form peroxides when exposed to air or light. Date these containers when new and dispose as hazardous waste within six months.

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- 4.2 Chemicals that are sensitive to peroxide formation can be broken into three categories (Jackson, J. Chem. Ed., 1970) as shown in the following table.
 - 4.2.1 Peroxide hazard after prolonged storage. Form potentially explosive peroxides without concentrating. All have been responsible for fatalities. Test for peroxide formation or discard after 3 months after opening.

4.2.2

isopropyl ether	divinyl acetylene
potassium metal	potassium amide
sodium amide	vinylidene chloride

The materials in this group are particularly hazardous and are capable of forming peroxides that may explode even without undergoing distillation or evaporation. One of the more dangerous is isopropyl ether, which decomposes rapidly on storage so that crystals of peroxides accumulate in the threads under the cap. This condition is extremely dangerous and the container should not be opened - friction may initiate detonation. Materials discovered in this condition may need to be removed by a bomb squad from the local fire department. These chemicals should never be stored for longer than 3 months; after this time they should be discarded without opening or should be tested for peroxide formation. Any container that has been stored for greater than 6 months should be approached with extreme caution.

4.2.3 Chemicals which become a peroxide hazard if concentrated, such as through distillation or evaporation. Test for peroxide formation or discard after 1 year.

dioxane	diethyl ether
tetrahydrofuran	acetal
cumene	cyclohexane
cyclopentene	diacetylene
dicyclopentadiene	ethylene glycol dimethyl ether
furan	methyl acetylene
methyl cyclopentane	methyl-isobutyl ketone
tetrahydronaphthalene	vinyl ethers

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The chemicals in this group should be discarded or tested for peroxide formation after 12 months. If the age of any of these compounds is unknown, or is suspected to be greater than these recommended time frames, the container should not be opened.

4.2.4 Chemicals which are a hazard due to peroxide initiation of polymerization. The peroxide forming potential increases for liquids of this group. Test for peroxide formation or discard after 1 year.

butadiene	chlorobutadiene
chlorotrifluoroethylene	styrene
tetrafluoroethylene	vinyl acetate
vinyl acetylene	vinyl chloride
vinyl pyridine	acrylonitrile

The chemicals in this group should be discarded or tested for peroxide formation after 12 months. If the age of any of these compounds is unknown, or is suspected to be greater than these recommended time frames, the container should not be opened.

5.0 PERSONAL PROTECTIVE EQUIPMENT

- **5.1** At minimum, safety glasses, lab coat, long pants, and closed toed shoes are to be worn when entering laboratories having hazardous chemicals.
- **5.2** Utilize shields and barricades, and personal protective equipment (such as face shields with throat protectors and heavy gloves) whenever there is a possibility of explosion or vigorous chemical reaction.
- **5.3** When handling hazardous chemicals or contacting potentially contaminated surfaces, protective gloves are to be worn.
- **5.4** Goggles (not safety glasses) are appropriate for processes where splash or spray is foreseeable.
- **5.5** For hazardous chemicals that are toxic via skin contact/ absorption, additional protective clothing (i.e., face shield, apron, over sleeves) is appropriate where chemical contact with body/skin is foreseeable.

6.0 Control of Hazards

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- 6.1 Minimize the quantity of peroxides kept in the lab.
- 6.2 Carefully review all cautionary material supplied by the manufacturer prior to use.
- 6.3 Segregate these compounds from others that could create a serious hazard to life or property should an accident occur.
- 6.4 Never return unused quantities back to the container (contamination!).
- 6.5 Cleanup all spills immediately.
- 6.6 Dilution of the organic peroxide with the appropriate inert solvent (aliphatic hydrocarbons, as an example) helps to reduce the sensitivity of the peroxide to shock and heat.
- 6.7 Avoid evaporation or distillation!
- 6.8 Avoid contact with any metal source, such as spatulas, because metals can promote explosive decomposition. Use Teflon coated or ceramic instead.
- 6.9 Ignition sources in the area of peroxide use must be prohibited.
- 6.10 All sources of friction and grinding must be avoided. This includes the use of glass containers with screw on caps (crystals may form in the threads) or glass stoppers (glass against glass friction).
- 6.11 Store peroxides at the lowest possible temperature consistent with their solubility or freezing point. Do not freeze or cause the peroxide to precipitate out, however, since this is the most dangerous state!

7.0 Disposal of Peroxide Forming Chemicals

- 7.1 Peroxide forming material that have been dated and are due for disposal, file a hazardous waste pickup request. EHS will schedule a pick up.
- 7.2 Never move a suspect container of peroxide forming material. Look at the material to determine the condition of the container. Stains, rust, deformed cans are all indication of age.
- 7.3 Call EHS to review the material.

8.0 CONTINGENCIES:

8.1 In case of a fire, explosion, or gas leak evacuate individuals from the area and call the emergency response (911). Notify supervision and adjacent personnel as quickly as possible. Observe appropriate procedures for personal injury or fire as provided in EHS Web site.

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8.2 In case of a chemical spill, alert others in the immediate vicinity and notify your supervisor. Determine the severity of the spill and proceed as appreciate. Small spills may be cleaned up by laboratory personnel. For spills outside of containment, fires, or explosion notify (578-5640) and Campus Police (911 or 578-3231). If possible to do so safely (without risk of over-exposure), take action to stop the release. Ensure that extraneous personnel remain at a safe distance until the spill is completely cleaned-up

9.0 REVIEWS AND REVISIONS:

This procedure shall be reviewed for compliance and effectiveness and revised as necessary on an annual basis.

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