Working with Peroxide-formers

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1 Introduction

This document offers a short and concise overview of the use of Peroxide-forming chemicals (PFCs). Understanding the following content is a crucial prerequisite in understanding basic safety fundamentals such as 1) hazard awareness, 2) engineering controls, 3) work practices, 4) PPE and 5) emergency response for working with Peroxide-formers chemicals.

2 Scope

The guideline applies to lab personnel, and it has been developed to assist them in the preparation of lab specific SOPs.

3 Procedure

3.1 Introduction to Peroxide-forming chemicals

PFCs are a class of compounds that can spontaneously form shock-sensitive explosive peroxide crystals by a free radical reaction of the hydrocarbon with oxygen. Practically they can "auto-oxidize" with atmospheric oxygen under ambient conditions to form organic peroxides (contains an -O–O- bond). Once formed, organic peroxides are sensitive to thermal or mechanical shock and tend to explode violently and can cause serious injury or death to researchers in the laboratory. Simply opening the container can initiate peroxide formation, while light and heat can act to accelerate the process. Under normal storage conditions, peroxides can accumulate in the chemical container and may explode when subjected to heat, friction or mechanical shock. The danger is increased when a PFC is concentrated by distillation or evaporation.

It is imperative that all researchers learn to recognize and safely handle peroxidizable chemicals.

3.2 Classes of PFCs

Different peroxidizable chemicals tend to form dangerous levels of peroxides at varying rates and under different conditions. PFCs fall under one of the following four classes (A - D) based on the time it takes to form explosive levels of peroxides:

Class A Chemicals that form explosive levels of peroxides without concentration. These are the most hazardous and can form test even explosive peroxide levels even if not opened.

Test every 3 months

Example: Isopropyl ether, Potassium metal, Potassium amide, Sodium amide, Vinylidene chloride, Divinylacetylene, Butadiene, Chloroprene, Tetrafluoroethylene, Tetrahydrofuran (THF) without inhibitor.

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Class B	Chemicals	that	form	explosive	levels	of	peroxides	after	
	concentration through evaporation or distillation.								

Test every 6 months

Example: Diethyl ether, 2-Propanol, 1,4-dioxane, Decalin, Cyclohexanol, Furan, Glyme, Diglyme, Isopropyl benzene, Tetralin, Tetrahydrofuran (THF) with inhibitor.

Class C	Chemicals that may auto polymerize as a result of peroxide formation. These materials are typically stored with polymerization inhibitors to prevent the polymerization reactions.	 Test If inhibited every 12 months If uninhibited every 24 hours
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Example: Styrene, Methyl methacrylate, Vinyl acetate, Vinyl chloride, Acrylonitrile, Vinyl pyridine

Chemicals that may form peroxides but cannot be clearly placed in Class A-C. Test peroxide levels quarterly. Test every 12 months

Storage Considerations 3.3

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Due to sunlight's ability to promote the formation of peroxides, all peroxidizable compounds (and in general all organic chemicals) should be stored away from heat and sunlight, tightly closed to limit exposure to oxygen and prevent evaporation, and segregated from incompatible hazard classes (e.g. oxidisers). Many manufacturers note that chemical bottle seals are only good for 2 years, so Class A, B, and C PFCs kept beyond this time limit must be disposed of.

- Store away from heat and ignition sources. Ensure containers are tightly sealed after each use and consider adding a blanket of an inert gas, such as nitrogen, to the container to help slow peroxide formation.
- Glass storage bottles should be amber, which blocks light.
- Designate a dedicated storage space in the cabinet for PFCs so none will be "forgotten" in the • back.
- Open bottles in order of receipt (FIFO: "first in first out") and finish open containers first.
- Store inhibitor-free chemicals under an inert atmosphere.
- PFCs should not be refrigerated at or below the temperature at which the peroxide-forming compound freezes or precipitates as these forms of peroxides are especially sensitive to shock and heat. Refrigeration does not prevent peroxide formation.
- As with any hazardous chemical, but particularly with PFCs, the amount of chemicals purchased and stored should be kept to an absolute minimum. Only order the amount of chemicals needed for the immediate experiment.

3.4 Labelling

The following information must be recorded on the label of all peroxide-forming chemicals:

Date received.

- Date opened.
- Peroxide test date (if open) and results.

Check For Peroxides Every 6 Months								
Opened	Test 1	Test 2	Test 3	Test 4				
Date								
Initials								

3.5 Testing

In KAUST each Class B peroxide-forming chemical container must be tested for peroxides when opened and at least every 6 months after that. The results of the peroxide test and the test date must be marked on the outside of the container.

The only exception is for the 2-Propanol which doesn't need to be routinely tested and labeled if only used for cleaning surfaces and DNA or RNA extraction (e.g. in biolabs). In these cases, it is not required to label the container with the opening date and then test every 6 months because the chemical is not distilled or concentrated.

Peroxide test strips can be purchased from the Chemical Warehouse or from a variety of safety supply vendors, such as VWR and Fisher Scientific. When using the test strips, if the strip turns blue, then peroxides are present. Light blue test results may be acceptable if your procedure does not call for concentrating, evaporating or distilling. Containers with darker blue test results must be deactivated or disposed of. You can test older test strips for efficacy with a dilute solution of hydrogen peroxide.



3.6 Disposal

- Peroxidized solvents may be disposed of in the same manner as the non-autoxidized solvent.
- Collect as hazardous waste following KAUST hazardous waste disposal procedure.
- Indicate the peroxide concentration on the request form.
- Don't mix peroxide-containing solvents with other waste streams.
- Ensure that the peroxidized solvent is not allowed to evaporate and thus concentrate the peroxide during handling and transport.

4 References

- SHA 3404-11R (2011) Laboratory Safety Guidance
- KAUST Laboratory Safety Manual
- ▶ HSE-RST-Chem001M Chemical Safety Program
- Wiley Guide to Chemical Incompatibilities
- > Handbook of reactive chemical hazards (Bretherick, Leslie Pitt, Martin J. Urben etc.)
- Prudent Practices in the Laboratory (2011)

5 Help

Questions about this guideline? Contact: hse@kaust.edu.sa