Chemical Safety Guidance Series

February 2020

Peroxides and Peroxide forming Chemicals

Occupational Health and Safety Service

HSD124C (rev4)

UNIVERSITY OF CAMBRIDGE

1. Peroxides

Peroxides are a group of compounds that contain an oxygen-oxygen bond.

As a class; organic peroxides are the most explosive substances that are normally found in the laboratory.

Peroxides are sensitive to light, heat, and friction, as well as to strong oxidizing and reducing agents. Explosions involving peroxides are unpredictable and violent.

Handling of Organic Peroxides

1. Store peroxides away from sources of light, heat, friction, and mechanical disturbance.
2. A solid peroxide can often be stored more safely if it is dissolved in a non-peroxidizable inert solvent such as an aliphatic hydrocarbon. Do not allow solutions of peroxides to evaporate, as the concentration of peroxide may reach a dangerous level. Regularly check the container to ensure solvent is not being lost.
3. Store solutions of peroxides at a cool temperature, **but do not refrigerate peroxides at a temperature below which precipitation or freezing out of solid material may occur**; in this form, peroxides are extremely sensitive to shock and heat.
4. DO NOT store peroxides or solutions of peroxides in glass bottles with ground glass or metal screw caps. The friction caused by opening the bottle can initiate an explosion. Polyethylene bottles with screw caps may be used.
5. Use ceramic spatulas for handling peroxides; metal spatulas can catalyze an explosive reaction.
6. DO NOT use naked flames in areas where peroxides are being handled.
7. Only purchase, store, and use the minimum quantity of peroxide necessary. Use special caution when scaling up reactions that use peroxides.
8. Perform experiments involving peroxides in a fume cupboard and behind a safety shield.
9. Clean up all spills immediately by absorption on vermiculite or other suitable absorbent. Transfer to a suitable container and dispose of as hazardous chemical waste.

2. Peroxide-forming Chemicals

Some chemicals can easily form peroxides when exposed to atmospheric oxygen through a process known as auto-oxidation. These peroxidizable chemicals are especially dangerous because the presence of peroxides may not be known as the rate of peroxide formation can vary and is very dependent upon the substance, the length of exposure to air and light, and container type: note ‘current’ manufacturers shelf life.

Peroxidized compounds can pose an explosion hazard under two situations:

1. When complex peroxides form a solid or precipitate in a peroxidizable liquid.
2. When a peroxidizable liquid is concentrated (by distillation, evaporation etc) leaving high concentrations of dissolved peroxides.

Handling of Peroxide-forming Chemicals

1. Buy and use only the minimum quantity of peroxidizable substance necessary.
2. Keep an inventory of peroxide-forming chemicals in the laboratory.
3. Store peroxide-forming chemicals for the shortest possible time and preferably no more than 6 months after opening. Date the container upon receipt and when it is opened and **NEVER keep peroxide forming chemicals longer than the date advised by the manufacturer.**

4. Test for peroxide formation when first opened and every 3 months. If peroxide levels are acceptable, date the container when the test was performed. If the material contains hazardous concentrations, either treat to remove peroxides or discard.
5. Peroxide formation in ethers and hydrocarbons can be prevented if they are stored under an inert atmosphere, for example, argon or nitrogen. The container should be well sealed.
6. Store peroxidizable chemicals away from sources of heat and light, ignition sources, mechanical shock, acids, bases and oxidisers.
7. NEVER return unused quantities back to the original container (contamination can accelerate peroxide formation).
8. Use or discard containers by the manufacturer's expiration date (if available).
9. Do not refrigerate peroxides if solid peroxide may precipitate or freeze out. Solid material is especially sensitive to shock.
10. Do not store peroxide-forming compounds in glass bottles having ground glass or metal screw caps, or metal cans with metal screw caps. Serious explosions can occur by merely unscrewing the top of a glass bottle that contains peroxides. Metal cans with plastic caps and polyethylene bottles are safer containers for ethers and other peroxidizable compounds. The safest container is the one supplied by the manufacturer.
11. NEVER attempt to force open a rusted or stuck cap on a container of a peroxide-forming chemical.
12. Test peroxidizable substances before using, and periodically in storage as specified in item 3 above. Tests include Quantofix Peroxide Test Papers (available from Aldrich).
13. Peroxides may be removed from solvents by passing the solvent through a column of alumina or Dowex-1 resin. The column MUST NOT be allowed to run dry and the packing should be handled as other peroxide waste. It is less dangerous, however, to use a new bottle of peroxide-free solvent than to purify solvent containing peroxides.
14. Serious accidents can occur when substances capable of forming peroxides are distilled. Consider other methods of purification. If distillation is necessary, the following precautions should be observed where peroxide formation is suspected.
    - Test for peroxides before distilling. The peroxide test strips can indicate the concentration of peroxide in ppm allowing you to know just how much peroxide is present.
    - Do the distillation under an inert atmosphere. Do not allow air to come in contact with hot solvent.
    - Add a suitable reducing agent to the distillation flask, such as sodium/benzophenone for ethers. Make sure that no compounds that react vigorously with the reducing agent are present in the distillation flask.
    - DO NOT carry the distillation to dryness; leave at least 10% liquid in the flask.
    - Wear goggles, face shield and use a free standing safety shield when distilling peroxidizable chemicals. Conduct the distillation in a fume cupboard with the sash fully closed.
    - Be aware that freshly distilled peroxidizable material may reform peroxide within two weeks of distillation.
15. Spills should be cleaned up immediately by absorption on solusorb or other suitable absorbents.
16. Always clearly label containers of peroxides or peroxide forming chemicals.
17. Safely dispose of peroxides or peroxide forming chemicals upon completion of a project, if there is no other **immediate** requirement for them.

Remember <u>NEVER</u> keep peroxide forming chemicals longer than the date currently advised by the manufacturer as shelf lives have been reduced in many cases.

3. Peroxidizable Compounds

Compounds that form Peroxides include:

1. Ethers and acetals. Especially dangerous are cyclic ethers (e.g. Tetrahydrofuran and dioxane) and ethers derived from primary and secondary alcohols, particularly diisopropyl ether. Ethers having an aromatic group bonded to the oxygen generally do not peroxidize under normal conditions.
2. Compounds containing benzylic hydrogen atoms, especially tertiary hydrogens, (e.g. cumene, tetralin).
3. Compounds containing allylic hydrogens (CH_2=$CHCH_2R$), including most alkenes (e.g. cyclohexene, cyclooctene).
4. Ketones, especially cyclic ketones.
5. Dienes and vinylacetylenes (e.g. divinylacetylene, butadiene).
6. Paraffinic and alkylaromatic hydrocarbons with tertiary hydrogens (e.g. decalin, methylcyclopentane).
7. Vinyl and vinylidene compounds (e.g., vinyl acetate, vinylidene chloride).
8. Aldehydes (particularly anhydrous acetaldehyde); ketones with an alpha- hydrogen (methyl isobutyl ketone); ureas, amides, lactams.
9. Potassium metal (actually forms the yellow superoxide KO_2) and alkali metal amides such as sodium amide.

Peroxidizable Compounds: Three Hazard Classification

- **Class A** includes compounds that form dangerous explosive peroxides after prolonged storage without concentration. These include diisopropyl ether, divinylacetylene, vinylidene chloride, potassium metal, and sodium amide.
- **Class B** includes compounds that readily form peroxides but are only dangerous when concentrated by evaporation or distillation. Examples are diethyl ether, dioxane, THF, tetralin, and cyclohexene.
- **Class C** includes monomers in which peroxide formation may initiate explosive polymerization. When stored in a liquid state. The peroxide forming potential dramatically increases. Examples are styrene, butadiene, and vinyl monomers.

HISTORY:
Reviewed with very minor modification 2020

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