

Guidelines for Explosive and Potentially Explosive Chemicals Safe Storage and Handling



University of California, Berkeley

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1. Introduction

Explosive chemicals can release tremendous amounts of destructive energy rapidly. If not handled properly, these chemicals can pose a serious threat to the health and safety of laboratory personnel, emergency responders, building occupants, chemical waste handlers, and disposal companies. For example, an explosion of old isopropyl ether killed a laboratory worker when he attempted to remove a glass stopper from the container.¹ In another instance, tetrazole exploded inside a hazardous waste incinerator, causing major damage and costly repairs.²

There are two classes of explosive chemicals. The first is known explosive chemicals that are designed and produced for use as an explosive (e.g., TNT, explosive bolts, bullets, blasting caps, and fireworks). The other class is potentially explosive chemicals (PECs), which include peroxidizable organic chemicals. Most chemicals that are used in research and teaching laboratories are stable and non-explosive at the time of purchase. Over time, some chemicals can oxidize, become contaminated, dry out, or otherwise destabilize to become PECs (e.g., isopropyl ether, sodium amide, and picric acid). See Appendix I—Explosive and Potentially Explosive Families— for examples.

Unlike known explosives, which are designed to be stable under normal conditions, PECs are particularly dangerous because they may explode if they are subjected to heat, light, friction, or mechanical shock. To handle and dispose of PECs properly, the University of California, Berkeley, campus uses a specialty contractor to transport the PEC to an isolated location where the chemical is opened by remote control. The contractor then stabilizes the chemical, making it safe to ship and dispose of. Costs can range from \$500 to \$1500 per chemical for this special handling service.

Note: There is a great deal of uncertainty regarding the hazards and safe handling of PECs. For example, with peroxide forming chemicals, there are no definite data available about the concentration and specific conditions at which these peroxides will detonate. Several common test methods may not detect all types of unstable peroxides, and some common deperoxidation procedures may not remove all types of unstable peroxides. Also, there are no specific federal Cal/OSHA regulations on this subject.

2. Common Laboratory PECs

There are many PECs used in academic research and teaching laboratories (see appendix I). The following are some commonly used chemicals that can become an explosion hazard under certain conditions:

- Organic chemicals that form peroxides through exposure to air or light (see Appendix II— Peroxide Forming Chemicals)
- Hydrated picric acid that becomes dry or becomes contaminated with metals that form metal picrate salts
- Sodium amide that reacts with air or moisture to form superoxides, as evidenced by yellow or brown discoloration
- Certain alkyl nitrates (e.g., butyl nitrate or propyl nitrate) that become contaminated with nitrogen oxides
- Certain normally stable perchlorates (e.g., pyridium perchlorate or tetraethylammonium perchlorate) that become unstable at elevated temperatures

Note: Most explosions occur while purifying or distilling mixtures. Therefore, use extreme caution before concentrating or purifying any mixture that may contain an explosive chemical (e.g., a peroxide forming chemical or perchlorate).

There is an additional group of chemicals that should be considered although they are not necessarily heat-, light-, friction-, or shock-sensitive. These chemicals give off gaseous degradation by-products that may cause over-pressurization of the container and explode. They can degrade over time and should be incorporated into a safety and handling system that will prevent them from becoming explosive hazards.

Contact EH&S immediately (642-3073) if you suspect a material is a PEC. Post warning signs so others do not handle or disturb the material. EH&S will inspect the chemical and devise an appropriate action plan to safely dispose of the chemical.

3. General Storage Precautions

It is important that chemical users track and dispose of chemicals before they become a problem. Proper inventory management systems can help mitigate risk to personnel and avert higher than normal disposal costs.

- Identify all explosive and potentially explosive chemicals in your inventory. Never store unlabeled chemicals. Before they can be shipped to a disposal site, unknown chemicals require special testing to determine which hazardous properties they possess. In some cases, an unknown chemical that is not a PEC could be classified as a PEC because its outward appearance resembles other known explosives. The handling and disposal of these chemicals costs significantly more than known chemicals.
- Record the opening date and the date that the chemical should be discarded on the label of chemicals that may degrade to become potentially explosive. Labels are available from EH&S or you may use the sample label on the next page.
- Keep explosive chemicals away from all ignition sources such as open flames, hot surfaces, spark sources, and direct sunlight.
- Consider designating a special area for explosive chemical use. Store explosive chemicals in an explosive magazine, and inspect areas weekly to comply with the California Fire Code. (Contact EH&S for assistance.)
- Periodically check containers of chemicals that could become over-pressurized, like highly concentrated formic acid (See Appendix III). Note: Release the pressure by unscrewing the cap, using protective heavy-duty gloves, chemically resistant coveralls, safety glasses, face shield, and a safety glass screen between you and the container.
- As part of your Chemical Hygiene Plan, make sure everyone who uses chemicals that are explosive or could become potentially explosive are thoroughly trained in safe storage methods, conditions to avoid (e.g., contamination), the hazards of the chemical, and disposal procedures.

4. Sample Label

Warning: May Form Explosive Peroxides

Store in tightly closed original container. Avoid exposure to light, air, and heat. If crystals, discoloration, or layering are visible, do not move or open the container. Contact EH&S immediately. Check for peroxides before distilling or concentrating.

This Chemical Has a Limited Shelf Life!

Date Received _____ Date Opened _____

Dispose of this chemical 18 months after receipt or 12 months after opening. See "Guidelines for Explosive and Potentially Explosive Chemicals Safe Storage and Handling" at www.ehs.berkeley.edu for specific expiration dates.

5. Specific Storage and Testing Guidelines for Peroxide Forming Chemicals

5.1 About Peroxide Forming Chemicals

Many oxygenated organic compounds become more and more dangerous upon prolonged storage because they tend to form explosive peroxides with age. Organic peroxides are carbon-based chemicals that contain the characteristic peroxide O-O bond. Peroxides may form in freshly distilled, undistilled, and unstabilized ethers within less than two weeks. Exposure to light and air enhances the formation of the peroxides. Many ethers tend to absorb and react with oxygen from the air to form unstable peroxides which may detonate with extreme violence when they become concentrated by evaporation or distillation. These ethers may also explode when combined with other compounds that produce a detonable mixture or when disturbed by heat, shock, or friction.

Peroxides formed in compounds by auto-oxidation have caused many accidents, including the unexpected explosions of the residue of solvents after distillation. While ethers present one of the most commonly known peroxidizable compound risks, other common solvents such as isopropanol have exploded upon distillation due to peroxide concentration.

While the peroxide formation potential in ethers is the primary hazard, ethers also pose inhalation hazards. Lower molecular weight ethers are powerful narcotics that can cause death in large doses.

With all peroxide forming chemicals it is preferable to use small containers that can be completely emptied, rather than take small amounts from a large container over time. Ethers should be stored in amber bottles or other opaque containers and under a blanket of inert gas, such as nitrogen or argon, or over a reducing agent to inhibit formation of peroxides. Containers of ether and other peroxide forming chemicals should be marked with the date they are opened and with the date of required disposal. Mark these dates on the container using an indelible marker or attach a PEC warning label (such as the sample in section 4 or the label shown on the cover of this booklet) and fill out the dates section. Labels are available from EH&S.

5.2 Testing Schedule for Peroxide Forming Chemicals

By the expiration date, the person using a peroxide forming chemical should either dispose of it or test it for peroxide content. Dispose of any chemicals found to have a peroxide concentration greater than or equal to 100 parts per million. Chemicals that have lasted beyond the recommended shelf life but have been tested and show no detectable peroxides, or whose peroxide concentrations are less than 100 ppm, may be retained but should be tested according to Table 1 below. Testing results should be recorded on the container. **Test all peroxide formers prior to distillation**, regardless of age.

Never test containers of unknown age or origin. Old bottles may contain concentrated peroxides, or peroxides may have crystallized in the cap threads, which would present a serious hazard when opening the bottle for testing. Call EH&S for managing old containers.

Disposal or Testing Recommendations

The following recommendations were obtained from *Prudent Practices for Disposal of Chemicals from Laboratories, Appendix I*, National Academy Press, Washington, DC, 1983, pp. 245-246.

Table 1

Storage and Disposal of Peroxidizable Organic Chemicals (See Appendix II for chemical lists A-D)

| <u>Peroxidizable Chemical Classification</u> | <u>Dispose or Test After*</u> |
|----------------------------------------------|-------------------------------|
| Unopened chemicals from the manufacture | 18 months |
| Opened containers | |
| List A chemicals | 3 months |
| List B chemicals | 12 months |
| List C, <i>uninhibited</i> chemicals | 24 hours |
| List C, <i>inhibited</i> chemicals | 12 months** |
| List D chemicals | 12 months |

* Never open or test containers of unknown origin or age, or those that have visible evidence of peroxides!

** Do not store under inert atmosphere.

5.3. An Analysis of Common Detection Procedures

The following pages are a reprint of part of R. J. Kelly's article, "Review of Safety Guidelines for Peroxidizable Organic Chemicals," originally published in *Chemical Health & Safety*. Kelly's references and a few passages (indicated by ellipses) have been omitted. (See References, page 11.)

Peroxide Detection Methods

Although there are numerous quantitative, semiquantitative, and qualitative methods to detect peroxides in organic and aqueous solutions, four are commonly used. They include two qualitative variations on the iodine detection method, the qualitative ferrous thiocyanate method, and the use of semiquantitative redox dip strips. Recently, the use of titanium sulfate has been suggested as a means to detect peroxides, but it is not widely used.

The dip strip method has the advantage of being the most gentle test, an important consideration if the chemical is shock sensitive. It also has another substantial advantage: It can detect, to some extent, dialkyl peroxide, polyperoxides, and cyclic peroxides, compounds that are not efficiently detected by the other methods (except, perhaps, the titanium sulfate method). Some solvents, notably isopropyl ether and dioxane, may form significant and hazardous levels of these higher reaction products. Furthermore, the standard peroxide removal procedures may remove all of the hydroperoxides but leave behind dangerous levels of alkyl peroxides, polyperoxides, and cyclic peroxides. The routine ferrous thiocyanate and iodine methods may yield a false negative in this case, but the dip strip test would likely detect the remaining peroxides, although perhaps not quantitatively. The dip strip method, however is difficult to use with water-immiscible, low-volatility chemicals.

Ferrous Thiocyanate Method

This qualitative method relies on the oxidation by peroxide of colorless ferrous thiocyanate (Fe^{2+}) to the red ferric thiocyanate (Fe^{3+}). One drop of reagent is added to one drop of the chemical to be tested. A barely discernible pink color indicates that peroxides are present at a concentration of about 10 ppm. A clear pink to cherry color suggests a concentration of about 20 ppm. A red color indicates a concentration of about 80 ppm, and a deep red indicates a concentration as high as 400 ppm.

The reagent is prepared by dissolving 9 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 50 ml 18% HCl. A little granulated zinc is added, followed by 5 g NaSCN. When the transient red color fades, an additional 12 g NaSCN is added, and the liquid is decanted from the unused zinc into a clean, stoppered bottle. The shelf life of this reagent is very limited.

This method is sensitive only to hydroperoxides; it will not detect most other peroxides. Note: Use only when you suspect hydroperoxides are present.

Iodide Tests

This is the most common qualitative test for adventitious peroxides. The two primary variations on this procedure involve the oxidation of iodide to iodine by the peroxide, with the resulting formation of a yellow to brown color.

Method A

In this method, 1 mL of the material to be tested is added to an equal volume of glacial acetic acid, to which approximately 0.1 g NaI or KI (10% wt/vol) has been added. A yellow color indicates a low concentration of peroxides (40—100 ppm as hydrogen peroxide). A brown color indicates a higher concentration of peroxide. Blanks must always be prepared. The test solution has a very short shelf life and will naturally result in high blank values if stored for any length of time. Variations on this method include the use of a 20% wt/vol reagent and hydrochloric acid instead of glacial acetic acid and the use of sulfuric acid. Heating is recommended to enhance detection of higher peroxides that may not be detected by the routine process.

In quantitative variations on this method, the liberated iodine is titrated with 0.1 M NaSCN. This degree of precision is usually unnecessary for routine testing, and these methods do not increase the sensitivity of the method to higher peroxides.

Method B

In this method, 1 mL of a freshly prepared 10% KI solution is added to 10 mL of the organic liquid in a 25-mL glass stoppered vial. A barely visible yellow color suggests a peroxide content of 10—50 ppm. A clear and definite yellow color indicates a concentration of about 100 ppm, and brown color indicates a higher concentration. Variations on this method include using a 20% KI solution and using a 1:1 solvent/reagent ratio. Some authors recommend vigorous shaking or mixing.

Comparison of Methods A and B

Method A is often faster than Method B. Up to 15 minutes may be required for formation of color using Method B, whereas the color usually forms in < 1 minute for Method A. For both procedures, the color formed is a function of the peroxide content and the chemical tested.

Some scientists disagree about the sensitivity of these methods to peroxides other than hydroperoxides. Burfield states that the method is sensitive only to hydroperoxides. Noller and Bolton indicate that the acidified Method A is sensitive to hydroperoxides, peroxyacids, diacyl peroxides, and some peroxide esters, but not to dialkyl and alkyl diene peroxides. Davies makes a similar statement. Noller and Bolton suggest that heating, perhaps with the addition of hydroiodic acid, may be necessary to detect these compounds. Mair and Graupner use a combination of glacial acetic acid and hydrochloric acid plus heat to detect all peroxides. These latter two procedures are complex reflux processes that require extensive experience in chemistry and substantial laboratory facilities.

Dip Strips

E. Merck and Aldrich Chemical companies make dip strips for the semi-quantitative detection of peroxides in organic and inorganic solutions, and they are available from many suppliers. The strip incorporates the enzyme peroxidase, which transfers oxygen from peroxide to an incorporated organic redox indicator. The indicator turns blue in the presence of peroxides. Comparison color scales are provided for organic and aqueous tests. The range for organic chemicals varies, depending on the manufacturer: 0—25 ppm for the Merck product and 1—100 ppm for Aldrich. Higher ranges can be accommodated by dilution of the suspect chemical with a miscible, non-peroxidized chemical.

For volatile organic chemicals, the test strip is immersed in the chemical for 1 second; then the tester breathes slowly on the test strip for 15—30 seconds, or until the color stabilizes. Vapor in the breath provides water for the reaction to proceed. The color is then compared with the scale provided on the bottle.

Modifications of this procedure are needed to test non-volatile organic compounds. The Aldrich strips have been successfully used as follows. For water-miscible compounds, add three drops of water to one drop of chemical to be tested. Wet the dip strip in the mixture, wait 2—3 minutes or until the color stabilizes, and multiply the result by 4. For water-immiscible compounds, mix three drops of a volatile ether with one drop of the low-volatility compound to be tested. Wet the dip strip and breathe on the reaction zone for 30—60 seconds, or until the color stabilizes, and multiply the measured value by 4.

These strips have a limited shelf life, but refrigeration is not recommended once the container has been opened, because repeated cooling and heating cause condensation that will ruin the strips. Storage under dry, inert atmosphere will prolong the shelf life.

Literature from E. Merck indicates that their test strips will detect hydroperoxides and most higher peroxides, but some polyperoxides may be poorly detected.

Titanium Sulfate

To detect organic peroxides, a solution of titanium sulfate in 50% sulfuric acid is used. When this reagent is added to a peroxidized solvent, a yellow-orange complex is formed. It has been stated that this method will detect higher peroxides, especially polyperoxides. The higher peroxides are hydrolyzed by the strong acid and are thereby made detectable.

The test reagent is prepared by dissolving a small amount of TiO_2 in hot concentrated sulfuric acid and adding this to an equal volume of water.

This method can only be recommended if it is compared by the user with other methods of known sensitivity and used accordingly.

Summary of Detection Methods

Dip strips provide the highest sensitivity and the most accurate quantification of peroxide concentration for routine testing. Furthermore, they are easier, faster, and safer to use than other methods, and they detect a wider range of peroxides than do other simple methods. They are, however, somewhat inconvenient to use for testing nonvolatile solvents, and they have a limited shelf life after the container is opened. . . .

Removal of Peroxides

In some cases, it might be desirable to remove peroxides from chemicals rather than dispose of the entire chemical. This can be done safely for relatively low levels of peroxides (less than 500 to 1000 ppm). Scrubbing of concentrations greater than 1000 ppm may pose an unacceptable hazard, depending on the chemical involved. Scrubbing of discolored, crystallized, or layered peroxide formers is almost certainly too hazardous and should not be attempted. These severely peroxidized compounds should be treated as potential bombs.

Method 1

Hydroperoxides can be removed by passing the solvent through a column of activated alumina. This method works for water-soluble and water-insoluble chemicals. The washed solvent should be retested to ensure that it has been cleaned adequately. The alumina apparently catalyzes the degradation of some peroxides, but in some cases the peroxide may remain intact on the alumina, making it potentially shock sensitive. The alumina can be deactivated by flushing with a dilute acid solution of potassium iodide or ferrous sulfate.

The amount of alumina required depends on the quantity of peroxide. As a start, a column containing 100 g of alumina should be used for 100 mL of solvent. More alumina or passage through a second column may be required to eliminate peroxides. This method is relatively slow and expensive, but it avoids shaking the solvent and does not add water. It will not reliably remove dialkyl peroxides, although there is some controversy about this.

Method 2

Peroxides in water-insoluble chemicals can be removed by shaking with a concentrated solution of ferrous salt; 60 g FeSO_4 , 6 mL concentrated H_2SO_4 , and 110 mL water are a standard solution. Another formulation is 100 g FeSO_4 , 42 mL concentrated HCl , and 85 mL water. The peroxide former is extracted two to three times with an equal volume of the reagent. Drying over sodium or magnesium sulfate can be used to remove dissolved water. Shaking should be very gentle for the first extraction. This method has been shown repeatedly to be quite effective for most peroxides, but it is not reliable for removing alkyl peroxides.

Method 3

Blue-indicating molecular sieve (4–8 mesh, type 4A) is added to containers of peroxidized chemicals and allowed to sit for 1–30 days. An amount equivalent to about 5%–10% (wt/vol) of the peroxidized liquid is used. Alternatively, the mixture can be refluxed, and the reaction occurs within 4 hours. The peroxide is broken down, and the indicator in the sieve is consumed. When run at room temperature, this process is apparently safe, slow, and controlled. Dialkyl peroxides are not efficiently removed, especially from dioxane. This method may be particularly suited to treatment of THF, diisopropyl ethers, and diethyl ethers, which may be decontaminated at room temperature in a couple of days.

Other methods for removing higher peroxides including dialkyl peroxides

In one suggested procedure, a 10% molar excess of sodium or potassium iodide is dissolved in 70 mL glacial acetic acid. A small quantity of 36% (wt/vol) HCl is added, followed by 0.01 mol of the dialkyl peroxide. The solution is heated to 90°C–100°C on a steam bath over the course of 30 minutes and held at that temperature for 5 hours. Zinc dissolved in acetic or hydrochloric acid has been recommended. Prolonged treatment with ferrous sulfate in 50% sulfuric acid has also been recommended.⁴

REFERENCES

- 1 *Journ. of Chem. Education* 1964, 41:(8) A 575-A579.
- 2 Illinois. Env. Protection Agency, *News*, Feb. 22, 1991, 91-117.
- 3 *Prudent Practices for Disposal of Chemicals from Laboratories*, Appendix I, National Academy Press, Washington, DC, 1983, pp. 245-246.
- 4 Kelly, R.J. "Review of Safety Guidelines for Peroxidizable Organic Chemicals," American Chemical Society—*Chemical Health & Safety*, 1996, 4(5), pp. 33-36. Used with permission.

Appendix I

Explosive and Potentially Explosive Chemical Families

Acetylene or acetylide compounds:

N-Chloro-3-aminopropyne
Propiolic acid
Propynethiol

Acyl azides

Acetyl azide
Cyanodiazocetyl azide
Phenylphosphonic azide chloride

Acyl hypohalites

Acetyl hypobromite
Hexafluoroglutaric dihypochlorite

Alkyl nitrates

Ethylidene dinitrate
Glyceryl trinitrate
Propyl nitrate

Alkyl perchlorates

Hexyl perchlorate
Ethyl perchlorate
1-Chloro-2-propyl perchlorate

Allyl trifluoromethanesulfonates

2-Chloro-2-propenyl trifluoromethanesulfonate

Amminemetal oxosalts

Ammonium hexanitrocobaltate
Bis(1,2-diaminoethane) diaquacobalt (III) perchlorate
Trihydrazine nickel (II) nitrate

Aromatic nitrates

Picric acid
Trinitrobenzene
Picryl sulfonic acid

Azides

Sodium azide
Lead azide
Hydrogen azide

Aziridines

1-Bromoaziridine

Azocarbaboranes

1,1'-Azo-1,2-dicarbadeborane

N-Azolum nitroimidates

Benzimidazolium 1-nitroimidate
4-Nitroamino-1,2,4-triazole
2-(N-Nitroamino)pyridine N-oxide

Diazo compounds

2-Buten-1-yl diazoacetate
Diethyl diazomalonate
Dinitrodiazomethane

Diazonium carboxylates, perchlorates, salts, sulfates, tetrahaloborates, and, triiodides

Benzenediazonium-2-carboxylate
4-Aminobenzenediazonium perchlorate
6-chloro-2,4-dinitrobenzenediazonium sulfate
2-Nitrobenzenediazonium tetrachloroborate
4-Toluenediazonium triiodide

Difluoroaminoalkanols

1,1-Difluorourea
Perfluoro-N-cyanodiaminomethane

Fluoro—nitro compounds

1-Fluoro-1,1-dinitrobutane
Fluorodinitromethyl azide

Fulminating metals

Lead fulminate
Gold fulminate
Silver fulminate

Furazan N-oxides

Dicyanofurazan N-oxide
4-Oximino-4,5,6,7-tetrahydrobenzofurazan N-oxide

Hydroxooxidiperoxochromate salts

1-Ammonium hydroxooxidiperoxochromate
Potassium hydroxooxidiperoxochromate

Iodine Compounds

Calcium 2-iodylbenzoate
Iodobenzene
2-Iodylvinyl chloride

Isoxazoles

3-Aminoisoxazole
3,5-Dimethylisoxazole

Metal Azide Halides

Chromyl azide chloride
Molybdenum diazide tetrachloride
Tungsten azide pentachloride

Metal Azides

Aluminum azide
Bis(cyclopentadienyl)tungsten diazide oxide
Mercury (I&II) azide
Sodium azide

N-Metal Derivatives

Cadmium nitride
Dibutylthallium isocyanate
Sodium amide

Metal Fulminates

Mercury (II) fulminate
Sodium fulminate
Tripropyllead fulminate

Metal Halogenates

Lead bromate

Metal Hydrides

Stibine (Antimony hydride)

Metal Nitrophenoxides

Lithium 4-nitrothiophenoxide
Potassium 4-nitrophenoxide

Metal Oxides

Bis (1-chloroethylthallium chloride) oxide
Magnesium chloride trioxide

Metal Oxohalogenates

Ammonium iodate
Lead acetate-lead bromate

Metal Oxometallates

Bis (benzene) chromium dichromate

Metal Perchlorates

Chromyl perchlorate

Metal Peroxides

Many transition metal peroxides are dangerously explosive.

Metal Peroxomolybdates

2-Potassium tetraperoxomolybdate
2-Sodium tetraperoxomolybdate

Metal Picramates

Palladium picramate
Uranyl picramate

Nitroaryl Compounds

N-Chloro-4-nitroaniline
Nitrogenous Base Nitrite Salts
Methylammonium nitrite

aci-Nitroquinonoid Compounds

Sodium 1,4-bis(aci-nitro)-2,5-cyclohexadienide

aci-Nitro Salts

Ammonium aci-nitromethanide
Dipotassium aci-dinitromethanide

Thallium aci-phenylnitromethanide

Nitroso Compounds

Dinitrosylnickel
Ehtyl N-methyl-N-nitrosocarbamate
Potassium nitrosodisulfate

N-S Compounds

Disulfur dinitride
Potassium sulfurdiimidate
Tetrasulfur tetranitride
Thiotrithiazyl nitrate

Organic Acids

Picric acid
Trinitroresorcinol

Organic Azides

Diazidomethyleneazine
Picryl azide
Vinyl azide

Organolithium Reagents

o-Trifluoromethyl phenyllithium
m-Bromo phenyllithium

Organomineral Peroxides

Bis(triethyltin) peroxide
Diethylhydroxotin hydroperoxide

Oximes

Bromoacetone oxime
Hydroxycopper glyoximate
Potassium cyclohexanehexone 1,3,5-trioximate

Oxosalts of Nitrogenous Bases

Ammonium tetranitroplatinate (II)
Diamminepalladium (II) nitrate
1,2-Diammonioethane nitrate

Ozonides

trans-2-Butene ozonide
Ethylene ozonide (1,2,4-trioxolane)
Trifluoroethylene ozonide

Perchlorate Salts of Nitrogenous Bases

Pyridinium perchlorate
Tetraethylammonium perchlorate
Perchloramide Salts
Barium perchloramide
Mercury (II) N-perchloryl benzylamide
Silver perchlorylamide

Perchloryl Compounds

2,6-Dinitro-4-perchlorylphenol
Perchloryl fluoride
N-Perchloryl piperidine

Peroxyacid salts

Calcium peroxodisulfate
Potassium tetraperoxomolybdate
Tetramethylammonium pentaperoxodichromate

Peroxyacids

Benzeneperoxyselemonic acid
Peroxyacetic acid
Peroxyformic acid

Peroxycarbonate esters

O-O-tert-Butyl isopropyl monoperoxycarbonate
Diallyl peroxydicarbonate
Dimethyl peroxydicarbonate

Phosphorus esters

Diethyl phosphite
Dibenzyl phosphorchloridate

Picrates

Nickel picrate (anhydrous)
S-7-Methylnonylthiuronium picrate
Sodium picrate

Platinum Compounds

Amminedeca-hydroxydiplatinum
cis-Diammineplatinum (II) nitrate
Trimethylplatinum hydroxide

Poly(dimercuryimmonium) Compounds

Poly(dimercuryimmonium picrate)
Poly(dimercuryimmonium permanganate)
Poly(dimercuryimmonium trinitrobenzoate)

Polymerization (violent)

Acrylic acid
Ethylene oxide
Vinyl acetate

Polynitroalkyl Compounds

Dinitroacetonitrile
Hexanitroethane
Potassium trinitromethanide

Polynitroaryl Compounds

5,6-Dinitro-2-dimethyl aminopyrimidinone
4-Nitro-1-picryl-1,2,3-triazole
2,4,6-Trinitrotolune

Silver Compounds

Silver nitride (fulminating silver)
Disilver ketenide
Phenylsilver
Silver azide
Silver Osmate

Strained-Ring Compounds

2-Azatricyclo[2.2.10^{2,6}]hept-7-yl perchlorate
Dicyclopropyldiazomethane
Prismane

Tetrazoles

5-Aminotetrazole
Silver and mercury salts of 5-nitrotetrazole
Tetrazole

Triazoles

3-Diazo-5-phenyl-3H-1,2,4-triazole
4-Hydroxy-3,5-dimethyl-1,2,4-triazole
1,2,3-Triazole

Appendix II

Common Peroxide-Forming Compounds

The following table lists some common peroxide-forming chemicals. For additional information about peroxides and peroxide-forming chemicals, refer to NFPA 43B, "Code for the Storage of Organic Peroxide Formulations" and Data Sheet I-655, Rev. 87, "Recognition and Handling of Peroxidizable Compounds" (National Safety Council). These documents are available from EH&S.

Table of Peroxidizable Chemicals

List A—Chemicals that may form explosive levels of peroxides without concentration by evaporation or distillation. These materials are particularly dangerous because they can be hazardous even if never opened.

Butadiene
 Chloroprene
 Divinylacetylene
 Isopropyl ether
 Tetrafluoroethylene
 Vinylidene Chloride

List B—Chemicals that form explosive levels of peroxides on concentration. They typically accumulate hazardous levels of peroxides only when evaporated, distilled or otherwise treated to concentrate the peroxides (e.g. deactivation or removal of peroxide inhibitors). Therefore, they have the potential of becoming far more hazardous after they are opened.

| | | | |
|----------------------|-------------------|------------------------|--------------------------|
| Acetal | Diacetylene | 3-Methyl-1-butanol | Tetrahydrofuran |
| Acetaldehyde | Dicyclopentadiene | Methylcyclopentane | Tetrahydronaphthalene |
| Benzyl alcohol | Diethyl ether | Methyl isobutyl ketone | Vinyl ethers |
| 2-Butanol | Diglyme | 4-Methyl-2-pentanol | Other secondary alcohols |
| Cumene | Dioxanes | 2-Pentanol | |
| Cyclohexanol | Glyme | 4-Penten-1-ol | |
| 2-Cyclohexen-1-ol | 4-Hepitanol | 1-Phenylethanol | |
| Cyclohexene | 2-Hexanol | 2-Phenylethanol | |
| Decahydronaphthalene | Methylacetylene | 2-Propanol | |

List C—Chemicals that may autopolymerize as a result of peroxide accumulation. These chemicals have been associated with hazardous polymerization reactions that are initiated by peroxides which have accumulated in solution. These materials are typically stored with polymerization inhibitors to prevent these dangerous reactions.

| | |
|-------------------------|---------------------|
| Acrylic acid | Vinyl acetate |
| Acrylonitrile | Vinylacetylene |
| Butadiene | Vinyl chloride |
| Chloroprene | Vinylpyridine |
| Chlorotrifluoroethylene | Vinylidene chloride |
| Methyl methacrylate | |
| Styrene | |
| Tetrafluoroethylene | |

List D represents other peroxidizable chemicals which can not be placed into the other categories but nevertheless require handling with precautions.

| | | | |
|-----------------------------------|------------------------------------|------------------------------------------|-----------------------------------|
| Acrolein | tert-Butyl methyl ether | Di(1-propynyl) ether | n-Methylphenetole |
| Allyl ether | n-Butyl phenyl ether | Di(2-propynyl) ether | 2-Methyltetrahydrofuran |
| Allyl ethyl ether | n-Butyl vinyl ether | Di-n-propoxymethane | 3-Methoxy-1-butyl acetate |
| Allyl phenyl ether | Chloroacetaldehyde diethylacetal | 1,2-Epoxy-3-isopropoxypropane | 2-Methoxyethanol |
| p-(n-Amyloxy)benzoyl chloride | 2-Chlorobutadiene | 1,2-Epoxy-3-phenoxypropane | 3-Methoxyethyl acetate |
| n-Amyl ether | 1-(2-Chloroethoxy)-2-phenoxyethane | | p-Ethoxyacetophenone |
| | | | 2-Methoxyethyl vinyl ether |
| Benzyl n-butyl ether | Chloroethylene | 1-(2-Ethoxyethoxy)ethyl acetate | Methoxy-1,3,5,7-cyclooctatetraene |
| | | | b-Methoxypropionitrile |
| Benzyl ether | Chloromethyl methyl ether | 2-Ethoxyethyl acetate | m-Nitrophenetole |
| Benzyl ethyl ether | b-Chlorophenetole | (2-Ethoxyethyl)-a-benzoyl benzoate | 1-Octene |
| Benzyl methyl ether | o-Chlorophenetole | 1-Ethoxynaphthalene | Oxybis(2-ethyl acetate) |
| Benzyl-1-naphthyl ether | p-Chlorophenetole | o,p-Ethoxyphenyl isocyanate | 1-Ethoxy-2-propyne |
| 1,2-Bis(2-chloroethoxy)ethane | Cyclooctene | 1-Ethoxy-2-propyne | b,b-Oxydipropionitrile |
| Bis(2-ethoxyethyl)ether | Cyclopropyl methyl ether | 3-Ethoxypropionitrile | 1-Pentene |
| Bis(2-(methoxyethoxy)ethyl) ether | Diallyl ether | 2-Ethylacrylaldehyde oxime | Phenoxyacetyl chloride |
| Bis(2-chloroethyl) ether | p-Di-n-butoxybenzene | 2-Ethylbutanol | a-Phenoxypropionyl chloride |
| Bis(2-ethoxyethyl) adipate | 1,2-Dibenzoyloxyethane | Ethyl-b-ethoxypropionate | Phenyl-o-propyl ether |
| | | | p-Phenylphenetone |
| Bis(2-methoxyethyl) carbonate | p-Dibenzoyloxybenzene | 2-Ethylhexanal | n-Propyl ether |
| Bis(2-methoxyethyl) ether | 1,2-Dichloroethyl ethyl ether | Ethyl vinyl ether | n-Propyl isopropyl ether |
| Bis(2-methoxyethyl) phthalate | 2,4-Dichlorophenetole | Furan | Sodium 8-11-14-eicosatetraenoate |
| Bis(2-methoxymethyl) adipate | Diethoxymethane | 2,5-Hexadiyn-1-ol | Sodium ethoxyacetylde |
| Bis(2-n-butoxyethyl) phthalate | 2,2-Diethoxypropane | 4,5-Hexadien-2-yn-1-ol | Tetrahydropyran |
| | | | Triethylene glycol diacetate |
| Bis(2-phenoxyethyl) ether | Diethyl ethoxymethylenemalonate | n-Hexyl ether | Triethylene glycol dipropionate |
| Bis(4-chlorobutyl) ether | Diethyl fumarate | o,p-Iodophenetole | 1,3,3-Trimethoxypropene |
| Bis(chloromethyl) ether | Diethyl acetal | Isoamyl benzyl ether | 1,1,2,3-Tetrachloro-1,3-butadiene |
| 2-Bromomethyl ethyl ether | Diethylketene | Isoamyl ether | 4-Vinyl cyclohexene |
| | | | Vinylene carbonate |
| beta-Bromophenetole | m,o,p-Diethoxybenzene | Isobutyl vinyl ether | Vinylidene chloride |
| o-Bromophenetole | 1,2-Diethoxyethane | Isophorone | |
| | | | |
| p-Bromophenetole | Dimethoxymethane | b-Isopropoxypropionitrile | |
| 3-Bromopropyl phenyl ether | 1,1-Dimethoxyethane | Isopropyl-2,4,5-trichlorophenoxy acetate | |
| 1,3-Butadiyne | Dimethylketene | Limonene | |
| Buten-3-yne | 3,3-Dimethoxypropene | 1,5-p-Methadiene | |
| tert-Butyl ethyl ether | 2,4-Dinitrophenetole | Methyl-p-(n-amyloxy)benzoate | |
| | 1,3-Dioxepane | 4-Methyl-2-pentanone | |

Appendix III

Chemicals that May Explode due to Over-pressurized Containers

(From M.J. Pitt and E. Pitt, *Handbook of Laboratory Waste Disposal*, Ellis Horwood Publisher, UK, 1985. Formic acid and phenol have been added to the list.) Note: This list may not be all-inclusive.

Aluminum chloride
Aluminum lithium hydride
Ammonia solution
Ammonium hydroxide
Ammonium persulfate
Anisyl chloride
Aqua regia
Benzenesulphonyl chloride
Bleach
Bleaching powder
Calcium carbide
Calcium hydride
Calcium hypochlorite
Chloroform
Chromic acid
Cumene hydroperoxide
Cyclohexene
Diethyl pyrocarbonate
Dimethylamine
Formic Acid
Hydrogen peroxide
Lauroyl peroxide
Lithium aluminum hydride
Lithium hydride
Nitric acid
Nitrosoguanidine
Peracetic acid
Phenol
Phosphorus trichloride
Potassium Persulphate
Silicon tetrachloride
Sodium borohydride
Sodium dithionite
Sodium hydride
Sodium hydrosulphite
Sodium hypochlorite
Sodium peroxide
Sodium persulphate
Thionyl chloride
Urea peroxide
Zinc