APPENDIX H

Classes of Peroxidizable Chemicals

A. Chemicals that form explosive levels of peroxides without concentration

Butadiene[a]
Chloroprene[a]
Divinylacetylene
Isopropyl ether
Tetrafluoroethylene[a]
Vinylidene chloride

B. Chemicals that form explosive levels of peroxides on concentration

Acetal
Acetaldehyde
Benzyl alcohol
2-Butanol
Cumene
Cyclohexanol
2-Cyclohexen-1-ol
Cyclohexene
Decahydronaphthalene
Diacetylene
Dicyclopentadiene
Diethyl ether
Diethylene glycol dimethyl ether (diglyme)
Dioxanes
Ethylene glycol dimethyl ether (glyme)
4-Heptanol
2-Hexanol
Methylacetylene
3-Methyl-1-butanol
Methylcyclopentane
Methyl isobutyl ketone
4-Methyl-2-pentanol
2-Penten-1-ol
4-Penten-1-ol
1-Phenylethanol
2-Phenylethanol
2-Propanol
Tetrahydroforan
Tetrahydronaphthalene
Vinyl ethers
Other secondary alcohols

C. Chemicals that may autopolymerize as a result of peroxide accumulation

Acrylic acid[b]
Acrylonitrile[b]
Butadiene[c]
Chloroprene[c]
Chlorotrifluoroethylene
Methyl methacrylate[b]
Styrene
Tetrafluoroethylene[c]
Vinyl acetate
Vinylacetylene
Vinyl chloride
Vinylpyridine
Vinyladiene chloride

D. Chemicals that may form peroxides but cannot clearly be placed in sections A-C

Acrolein
Allyl ether[d]
Allyl ethyl ether
Allyl phenyl ether
p-(n-Amyloxy)benzoyl chloride
n-Amyl ether
Benzyl n-butyl ether[d]
Benzyl ether[d]
Benzyl ethyl ether[d]
Benzyl methyl ether
Benzyl 1-naphthyl ether[d]
1,2-Bis(2-chloroethoxy)ethane
Bis(2-ethoxyethyl) ether
Bis(2-(methoxyethoxy)ethyl) ether
Bis(2-chloroethyl) ether
Bis(2-ethoxyethyl) adipate
tert-Butyl methyl ether
n-Butyl phenyl ether
n-Butyl vinyl ether
Chloroacetaldehyde diethylacetal[d]
2-Chlorobutadiene
1-(2-Chloroethoxy)-2-phenoxyethane
Chloroethylene
Chloromethyl methyl ether[e]
ß-Chlorophenetole
o-Chlorophenetole
p-Chlorophenetole
Cyclooctene[d]
Cyclopropyl methyl ether
Diallyl ether[d]
p-Di-n-butoxybenzene
1,2-Dibenzyloxyethane[d]
Di(1-propynyl) ether[f]
Di(2-propynyl) ether
Di-n-propoxymethane[d]
1,2-Epoxy-3-isopropoxypropane[d]
1,2-Epoxy-3-phenoxypropane
Ethoxyacetophenone
1-(2-Ethoxyethoxy)ethyl acetate
2-Ethoxyethyl acetate
(2-Ethoxyethyl)-o-benzoyl benzoate
1-Ethoxynaphthalene
o,p-Ethoxyphenyl isocyanate
1-Ethoxy-2-propyne
3-Ethoxyopropionitrile
2-Ethylacrylaldehyde oxime
2-Ethylbutanol
Ethyl ß-ethoxypropionate
4-Methyl-2-pentanone
n-Methylphenetole
2-Methyltetrahydrofuran
3-Methoxy-1-butyl acetate
2-Methoxyethanol
3-Methoxyethyl acetate
2-Methoxyethyl vinyl ether
Methoxy-1,3,5,7-cyclooctatetraene
ß-Methoxypropionitrile
m-Nitrophenetole
1-Octene
Oxybis(2-ethyl acetate)
Oxybis(2-ethyl benzoate)
ß,ß-Oxydipropionitrile
1-Pentene
Phenoxyacetyl chloride

Table D Continued

D. Chemicals that may form peroxides but cannot clearly be placed in sections A-C

Bis(2-ethoxyethyl) phthalate
Bis(2-methoxyethyl) carbonate
Bis(2-methoxyethyl) ether
Bis(2-methoxyethyl)phthalate
Bis(2-methoxymethyl) adipate
Bis(2-n-butoxyethyl) phthalate
Bis(2-phenoxyethyl) ether
Bis(4-chlorobutyl) ether
Bis(chloromethyl) ether[e]
2-Bromomethyl ethyl ether
ß-Bromophenetole
o-Bromophenetole
p-Bromophenetole
3-Bromopropyl phenyl ether
1,3-Butadiyne
Buten-3-yne
tert-Butyl ethyl ether
p-Dibenzyloxybenzene[d]
1,2-Dichloroethyl ethyl ether
2,4-Dichlorophenetole
Diethoxymethane[d]
2,2-Diethoxypropane
Diethyl ethoxymethylenemalonate
Diethyl fumarate[d]
Diethyl acetal[d]
Diethylketene[f]
m,o,p-Diethoxybenzene
1,2-Diethoxyethane
Dimethoxymethane[d]
1,1-Dimethoxyethane[d]
Dimethylketene[f]
3,3-Dimethoxypropene
2,4-Dinitrophenetole
1,3-Dioxepane[d]
2-Ethylhexanal
Ethyl vinyl ether
Furan
2,5-Hexadiyn-1-ol
4,5-Hexadien-2-yn-1-ol
n-Hexyl ether
o,p-Iodophenetole
Isoamyl benzyl ether[d]
Isoamyl ether[d]
Isobutyl vinyl ether
Isophorone[d]
p-Isopropoxypropionitrile[d]
Isopropyl 2,4,5-trichlorophenoxy-acetate
Limonene
1,5-p-Methadiene
Methyl p-(n-amyloxy)benzoate
å-Phenoxypropionyl chloride
Phenyl o-propyl ether
p-Phenylphenetone
n-Propylether
n-Propyl isopropyl ether
Sodium 8,11,14-eicosa tetraenoate
Sodium ethoxyacetylide[f]
Tetrahydropyran
Triethylene glycol diacetate
Triethylene glycol dipropionate
1,3,3-Trimethoxypropene[d]
1,1,2,3-Tetrachloro-1,3-butadiene
4-Vinyl cyclohexene
Vinylenecarbonate
Vinylidene chioride[d]

[a] When stored as a liquid monomer
[b] Although these chemicals form peroxides, no explosions involving these monomers
[c] When stored in liquid form, these chemicals form explosive levels of peroxides without concentration. They may also be stored as a gas in gas cylinders. When stored as a gas, these chemicals may autopolymerize as a result of peroxide accumulation.
[d] These chemicals easily form peroxides and should probably be considered under part B.
[e] OSHA-regulated carcinogen
[f] Extremely reactive and unstable compound.

Safe Storage Period for Peroxide Forming Chemicals

Description	Period
Unopened chemicals from manufacturer	18 months
Opened containers	
Chemicals in Part A	3 months
Chemicals in Parts B and D	12 months
Unihibited chemicals in Part C	24 hours
Inhibited chemicals in Part C	12 months[a]

[a] Do not store under inert atmosphere, oxygen required for inhibitor to function.

Sources: Kelly, Richard J., Chemical Health & Safety, American Chemical Society, **1996,** Sept, 28-36

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DETECTION AND INHIBITION OF PEROXIDES
BASIC PROTOCOLS

Ferrous Thiocyanate Detection Method

Ferrous thiocyanate will detect hydroperoxides with the following test:

1. Mix a solution of 5 ml of 1% ferrous ammonium sulfate, 0.5 ml of 1N sulfuric acid and 0.5 ml of 0.1N ammonium thiocyanate (if necessary decolorize with a trace of zinc dust)

2. Shake with an equal quantity of the solvent to be tested

3. If peroxides are present, a red color will develop

Potassium Iodide Detection Method

1. Add 1 ml of a freshly prepared 10% solution of potassium iodide to 10 ml of ethyl ether in a 25 ml glass-stoppered cylinder of colorless glass protected from light (both components are clear)

2. A resulting yellow color indicates the presence of 0.005% peroxides

Inhibition of Peroxides

1. Storage and handling under an inert atmosphere is a useful precaution

2. Addition of 0.001% hydroquinone, diphenylamine, polyhydroxyphenols, aminophenols or arylamines may stabilize ethers and inhibit formation of peroxides.

3. Dowex-1® has been reported effective for inhibiting peroxide formation in ethyl ether.

4. 100 ppm of 1-naphthol effective for peroxide inhibition in isopropyl ether.

5. Hydroquinone effective for peroxide inhibition in tetrahydrofuran.

6. Stannous chloride or ferrous sulfate effective for peroxide inhibition in dioxane.

Peroxides Test Strips

These test strips are available from EM Scientific, cat. No. 10011-1 or from Lab Safety Supply, cat. No. 1162. These strips quantify peroxides up to a concentration of 25 ppm. Aldrich Chemical has a peroxide test strip, cat. No. Z10,168-0, that measures up to 100 ppm peroxide. The actual concentration at which peroxides become hazardous is not specifically stated in the literature. A number of publications use 100 ppm as a control value for managing the material safely.

Please note that these methods are BASIC protocols. Should a researcher perform one of these methods, all safety precautions should be thoroughly researched.

Sources:
1. Furr, Keith Handbook of Lab Safety, 4th ed., CRC Press, 1995
2. Kelly, Richard J., Review of Safety Guidelines for Peroxidizable Organic Chemicals, Chemical Health & Safety, American Chemical Society, Sept./Oct 1996