Appendix 7 – Peroxide Forming Chemicals

The following lists of chemicals are not exhaustive. Principal Investigators must consult the MSDSs and other information sources for the chemicals used in their work areas to determine the potential for peroxide-formation.

List A: Chemicals that form explosive levels of peroxides without concentration
(Safe storage limit - 3 months)

Chemical Name	CAS	Synonyms	State
Butadiene (1)	106-99-0	1,3-Butadiene	l
Chloroprene (1)	126-99-8	2-Chloro-1,3- butadiene	l
Divinyl acetylene	821-08-9	1,5-Hexadien- 3-yne	l
Isopropyl ether	108-20-3		l
Tetrafluoroethylene (1)	116-14-3		l
Vinyl ether	109-93-3	Divinyl ether	l
Vinylidene chloride	75-35-4	1,1- Dichloroethylene	l

List B: Chemicals that form explosive levels of peroxides on concentration
(Safe storage time - 12 months)

Chemical Name	CAS	Synonyms	State
Acetal	105-57-7		l
Acetaldehyde	75-07-0		l
Benzyl alcohol	100-51-6		l
2-Butanol**	78-92-2		l
Cyclohexanol	108-93-0		l
Cyclohexene	110-83-8		l
2-Cyclohexen-1-ol	822-67-3		l
Cyclopentene	142-29-0		l
Decahydronaphthalene	91-17-8		l
Diacetylene	460-12-8		g
Dicyclopentadiene	77-73-6		l
Diethylene glycol dimethyl ether	111-96-6	Diglyme	l
Dioxane	123-91-1	1,4-Dioxane	l
Ethylene glycol dimethyl ether	110-71-4	Glyme	l
Ethyl ether	60-29-7	Diethyl ether	l
Furan	128-37-0		l
4-Heptanol	589-55-9		l
2-Hexanol**	626-93-7		l
Isopropyl benzene	98-82-8	Cumene	l
Methyl acetylene	74-99-7	Propyne	g
3-Methyl-1-butanol	123-51-3	Isoamyl alcohol	l
Methyl cyclopentane	96-37-7		l
Methyl isobutyl ketone	108-10-1	Methyl-i-butyl ketone	l
4-Methyl-2-pentanol	108-11-2		l
2-Pentanol**	6032-29-7		l
4-Penten-1-ol	821-09-0		l
1-Phenylethanol	98-85-1	alpha-Methyl-benzyl alcohol	l
2-Phenylethanol	60-12-8	Phenethyl alcohol	l
Tetrahydrofuran	109-99-9		l
Tetrahydronaphthalene	119-64-2		l

List C: Chemicals that may autopolymerize as a result of peroxide accumulation
(Safe storage time: inhibited chemicals - 12 months; uninhibited chemicals: - 24 hours)

Chemical Name	CAS	Synonyms	State
Acrylic acid (2)	79-10-7		l
Acrylonitrile (2)	107-13-1		l
Butadiene (3)	106-99-0		g
Buten-3-yne	689-97-4	Vinyl acetylene & Butenyne	g
Chloroprene (3)	126-99-8	2-Chloro-1,3-butadiene	g
Chlorotrifluoroethylene	79-38-9		g
Methyl methracrylate (2)	80-62-6		l
Styrene	100-42-5		l
Tetrafluoroethylene (3)	116-14-3		g
Vinyl acetate	108-05-4		l
Vinyl chloride	75-01-4	Mono-chloroethylene	g
Vinylidene chloride	75-35-4	1,1-Dichloroethylene	l
2-Vinyl pyridine	100-69-6		l
4-Vinyl pyridine	100-43-6		l

Notes: ** Please note that secondary alcohols can be peroxide-forming chemical hazards. However, this is true only for the anhydrous form of the alcohols, and it is also only true if they are used in chemical processes (e.g., heating, distilling, performing chemical reactions, performing bulk evaporations). If these chemicals are used only for wipe cleaning or solvent extractions, there is no evidence that these secondary alcohols are dangerous.

1. When stored as a liquid monomer.
2. Although these form peroxides, no explosions involving these monomers have been reported.
3. When stored as a gas in gas cylinders.

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

Chemical Name	CAS	Chemical Name	CAS
Acrolein	107-02-8	Isobutyl vinyl ether	109-53-5
Allyl ether	557-40-4	Isophrone	78-59-1
Allyl ethyl ether	537-31-3	b-Isoproxypropionitile	
Allyl phenyl ether	1746-13-0	tert-Butyl methyl ether	16634-04-0
p-(n-Amyloxy)benzoyl chloride	36823-84-4	n-Butyl phenyl ether	1126-79-0
n-Amyl ether	693-65-2	n-Butyl vinyl ether	11-34-2
Benzyl n-butyl ether	3459-80-1	Chloroacetaldehyde diethylacetal	621-62-5
Benzyl ether	103-50-4	2-Chlorobutadiene	126-99-8
Benzyl ethyl ether	539-30-01	1-(2-Chloroethoxy)-2-phenoxyethane	2243-49-91
Benzyl methyl ether	558-86-3	Chloroethylene	75-01-4
Benzyl-1-napthyl ether	613-62-7	Chloromethyl methyl ether	107-30-2
1,2-Bis(2-chloroethoxyl)ethane	112-26-5	b-Chlorophenetole	614-72-2
Bis(2-ethoxyethyl)ether	112-36-7	o-Chorophenetole	
Bis(2-(methoxyethoxy)ethyl) ether	143-24-8	Cyclooctene	931-88-4
Bis(2-chloroethyl) ether	111-44-4	Cyclopropyl methyl ether	540-47-6
Bis(2-ethoxyethyl) adipate	109-44-4	Diallyl ether	557-40-4
Bis(2-methoxyethyl) carbonate		p-Di-n-butoxybenzene	75942-37-9
Bis(2-methoxyethyl) ether	119-96-6	1,2-Dibenzyloxyethane	
Bis(2-methoxyethyl) phthalate	117-82-8	p-Dibenzyloxybenzene	
Bis(2-methoxymethyl) adipate	106-06-3	1,2-Dichloroethyl ethyl ether	623-46-1
Bis(2-n-butoxyethyl) phthalate	117-83-9	2,4-Dichlorophenetole	5392-86-9
Bis(2-phenoxyethyl) ether	622-87-7	Diethoxymethane	462-95-3
Bis(4-chlorobutyl) ether	6334-96-9	2,2-Diethoxypropane	126-84-1

Bis(chloromethyl) ether	542-88-1	Diethyl ethoxymethylenemalonate	87-13-8
2-Bromomethyl ethyl ether	13057-17-5	Diethyl fumarate	623-91-6
beta-Bromophenetole	596-10-6	Diethyl acetal	105-57-7
o-Bromophenetole	593-19-7	Diethylketone	96-22-0
p-Bromophenetole		m,o,p-Diethoxybenzene	2168-54-9
3-Bromopropyl phenyl ether	588-63-6	1,2-Diethoxyethane	629-14-1
Di(1-propynl) ether	111-43-4	Dimethoxymethane	109-87-5
Di(2-propynl) ether		1,1-Dimethoxyethane	534-15-6
Di-n-propoxymethane	505-84-0	n-Methylphenetole	
1,2-Epoxy-3-isopropoxypropane		2-Methyltetrahydrofuran	202-507-4
1,2-Epoxy-3-phenoxypropane	122-60-1	3-Methoxy-1-butyl acetate	4435-53-4
p-Ethoxyacetophenone	11676-63-7	2-Methoxyethanol	109-86-4
1-(2-Ethoxyethoxy)ethyl acetate		3-Methoxyethyl acetate	110-49-6
2-Ethoxyethyl acetate	111-15-9	2-Methoxyethyl vinyl ether	111-96-6
(2-Ethoxyethyl)-a-benzoyl benzoate		Methoxy-1,3,5,7-cyclooctatetraene	
1-Ethoxynaphthalene	5328-01-8	b-Methoxypropionitrile	110-67-8
o,p-Ethoxyphenyl isocyanate	5395-71-1	m-Nitrophenetole	
1-Ethoxy-2-propyne		1-Octene	203-893-7
3-Ethoxypropionitrile	2141-62-0	Oxybis(2-ethyl acetate)	
2-Ethylacrylaldehyde oxime		Oxybis(2-ethyl benzoate)	
2-Ethylbutanol	97-75-0	b,b-Oxydipropionitrile	
Ethyl-b-ethoxypropionate	763-69-9	1-Pentene	203-694-5
2-Ethylhexanal	123-05-7	Phenoxyacetyl chloride	211-862-4
Ethyl vinyl ether	109-92-2	2-Phenoxypropionyl chloride	122-35-0
Furan	110-100-9	Phenyl-o-propyl ether	
2,5-Hexadiyn-1-ol		p-Phenylphenetone	
4,5-Hexadien-2-yn-1-ol		n-Propyl ether	111-43-7
n-Hexyl ether	112-58-3	n-Propyl isopropyl ether	
Isoamyl benzyl ether		Sodium 8-11-14-eicosatetraenoate	
Isobutyl vinyl ether	109-53-5	Sodium ethoxyacetylide	
Isophorone	78-59-1	Tetrahydropyran	142-68-7
Isoamyl ether	544-01-4	Triethylene glycol dipropionate	
b-Isopropoxypropionitrile		1,3,3-Trimethoxypropane	241-547-7
Isopropyl-2,4,5-trichlorophenoxy acetate		1,1,2,3-Tetrachloro-1,3-butadiene	921-09-5
		4-Vinyl cyclohexene	100-40-3
		Vinylene carbonate	

Source: Kelly, R.J., Review of Safety Guidelines for Peroxidizable Organic Chemicals, Chemical Health and Safety, September/October, 1996.

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, Revised 12/97

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

0. 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)
1. 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

A set of peroxides test strips can be found by a number of manufacturers. 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 and purchased test strips should be able to detect this level.

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