



ORGANIC PEROXIDES

Organic Peroxides – Their Safe Handling and Use



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INTRODUCTION

The purpose of this bulletin is to provide information on the safe handling and use of organic peroxides.

Chemically, organic peroxides are compounds characterized by the presence of an oxygen-oxygen linkage in the molecular structure.

Organic peroxides are sensitive to heat and contamination, since these conditions will cleave the oxy-oxy bonds to form free radicals. Since organic peroxides are reactive chemicals, they can be dangerous if mistreated or mishandled.

In case of Emergency call – Chemtrec: 800-424-9300

For Medical Assistance call – R.M.P.C.C.: 303-623-5716 (Rocky Mt. Poison Control Center)

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SAFETY GUIDELINES/TYPES OF ORGANIC PEROXIDES

A wide variety of organic peroxides are now offered commercially to meet the sophisticated needs of polymer manufacturers. Among them are peroxyesters, peroxydicarbonates, dialkyl peroxides, diacyl peroxides, hydroperoxides, peroxyketals and MEK peroxides. Products representing each of these classes are listed in Table 1. (Note: MEK or Ketone peroxides are a mixture of peroxides and hydroperoxides).

There are differences in the degree and type of hazard associated with these peroxides. A series of tests has been carried out to evaluate properties such as shock sensitivity, heat sensitivity, burning rate, flash point and storage stability. The results of the tests have proven helpful in establishing safe handling, storage and disposal guidelines, and in developing the packaging and shipping procedures described in this bulletin.

Table 1	Represen	tative organ	ic peroxides
Table I	ricpresen	tative organi	io peroxides

Peroxyesters	Peroxydicarbonates	Dialkyl Peroxides	Diacyl Peroxides	Hydroperoxides	Peroxyketals	Ketone Peroxides
0 R-00C-R	0 0 R-0C-00-C0-R	R-00-R	0 0 R-C-00-C-R	R-OOH	R'OO OOR' R-C-R	
Luperox P (t-Butyl perbenzoate)	Luperox 223-M75S (Di-2-ethylhexyl peroxydicarbonate)	Luperox DI (Di-t-Butyl peroxide)	Luperox A98 (Benzoyl peroxide)	Luperox TBH70X (t-Butyl hydroperoxide)	Luperox 231 (1,1-Di(t-Butyl peroxy) 3,3,5-trimethyl cyclohexane)	Luperox DDM-9 (MEKP Solution in Plasticizer - 9% Active Oxygen)
Luperox® 26 (t-Butyl peroctoate)	Luperox 225-M60S (Di-sec-Butyl peroxydicarbonate)	Luperox 101 2,5-dimethyl-2,5-bis (t-Butyl-peroxy) hexane	Luperox LP (Lauroyl peroxide)	Luperox CU90 (Cumene hydroperoxide)	Luperox 331M80 1,1-Di (t-Butyl peroxy) cyclohexane	Luperox Delta-X9 (MEKP Solution in Plasticizer - 9% Active Oxygen)
Luperox 11M75 (t-Butyl peroxypivalate)		Luperox DC (Dicumyl peroxide)				Luperox DHD-9 (MEKP Solution in Plasticizer - 9% Active Oxygen)
Luperox 10M75 (t-Butyl peroxy neodecanoate)		Luperox F (2,2-bis (t-butyl peroxy) diisopropylbenzene(s))				Luperox 224 (2,4 Pentanedione Peroxide Solution in Plasticizer)

Note: Lupersol® DDM-9*, DHD-9*, DDM-30* and Delta X-9* will change to Luperox and drop * during 2001. Formulations will not change.

The major causes of peroxide decomposition (sources of hazard) are Heat, Fire, Friction, Shock and Contamination. Examples of the common sources of these include:

Heat - Sunlight; loss of refrigeration; radiators; heating elements; hot reaction vessels; heating ducts.

Fire - Open flame; sparks.

Friction - Mixing; pumping; grinding; traffic over spillage (which can generate heat).

Shock - Dropping; impact during transportation (which can generate heat).

Contamination - Metal salts; amines; acids; bases; polymerization accelerator; transition metals; persulfates.

The major safety characteristics Arkema Inc. measures to determine the relative hazard of an organic peroxide include: shock sensitivity, the amount of energy released during a decomposition, and flash point. Also measured are the ease of burning, sensitivity to rate of heat rise, thermal stability, self accelerating decompostion temperature and ignition or autoignition characteristics.

STANDARD SAFETY TESTS

Standard tests have been developed for determining the hazard of peroxides. The following is a list and description of these established tests:

A.SADT (Self Accelerating Decomposition Temperature)

The SADT test establishes the lowest temperature at which a peroxide, in its largest commerical package, will undergo self accelerating decomposition. The type of decomposition and damage potential are measured, and the severity of decomposition is determined. The two parameters having the

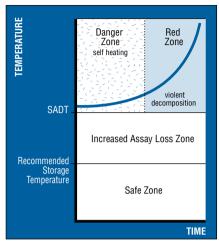


Figure 1

greatest effect on SADT are rate of decomposition and heat loss from the package. Figure 1 illustrates the impact of the SADT.

B. Shock Sensitivity

A standard weight is dropped on a small sample in an "impact tester". The height of the fall required for the weight to decompose the product is a measure of its sensitivity to shock. Dry/pure Dibenzoyl peroxide (Luperox® A98) is one of the few commercially available peroxides to exhibit shock sensitivity in this test.

C. Flash Point

The standard (closed cup) SETA flash test is now used. It is the temperature at which the product vapors ignite on contact with an open flame.

D. Thermal Stability Test

Results are determined by storing peroxide at a constant temperature for a specified time. The results of this test in terms of weight loss and assay are used as criteria for establishing storage temperature and shelf life requirements.

Product descriptions and safety data for representative organic peroxide formulations are given in tables 2 and 3.

HAZARD OVERVIEW

The three primary types of hazards to be concerned with are flammability, heat sensitivity and contamination.

The following statements are provided as general discussion for these types of hazards, as they relate to all organic peroxides.

A. Flammability

All organic peroxides will burn vigorously, and once ignited will be difficult to extinguish.

The flammability of organic peroxides will also be affected by the decomposition products. When most peroxides begin to decompose they will generate vapors and heat. Such vapors may be flammable and could be the cause of an explosion.

B. Heat Sensitivity

All organic peroxides are sensitive to heat. If a peroxide is heated above a certain temperature (depending on the specific heat sensitivity of the peroxide itself) the rate of decompostion will increase in an uncontrolled manner. This reaction can become violent, releasing large volumes of hot, flammable gasses.

The temperature at which this will occur depends on the volume of the peroxide, the container and the period of time the peroxide remains at that temperature. The self accelerating decomposition temperature (SADT) test provides a measure of this hazard.

In general, the best way to avoid decomposition due to heat is to scrupulously adhere to the recommended storage temperatures for each product. This is particularly true for peroxides requiring refrigerated storage.

C. Contamination

Chemical contamination can accelerate decomposition of organic peroxides. Care should be taken to avoid all forms of contamination, particularly oxidizing and reducing agents and metal salts – especially strong mineral acids. These will initiate a rapid decomposition at normal ambient temperatures, while many heavy metals such as copper, iron, brass, etc. will have a similar effect over a longer period of time.

Trade Name	Peroxide Name	Physical Form	Diluent	Assay (%)	Max. Storage Temp °F (C°)	SADT	NFPA Code 704 Health Hazard ID.	NFPA Code 704 Flamm. Hazard ID.	NFPA Code 704 Reactivity Hazard ID.	NFPA Cod 432 Storag Class
I uperox® I P	Dilaurovi Peroxide	Solid	AN	98.50%	27° C/80° F	51° C (65#ctn)	-	2	2	IV (110 lb.)
Luperox A98	Dibenzoyl Peroxide	Solid	NA	%86	38° C/ 100° F	68° C (1#ctn.)		· co	4	I (1lb.)
Luperox A75	Dibenzoyl Peroxide	Solid	Water	75%	38° C /100° F	71° C (25# ctn)	1	2	2	III (25 lb.)
Luperox A75FP	Dibenzoyl Peroxide	Solid USP Grade	Water	75%	38° C /100° F	71° C (25# ctn.)		2	2	III (25 lb.)
Luperox A70S	Dibenzoyl Peroxide	Solid USP Grade	Water	70%	38° C/100° F	82° C (50# ctn)	,	2	2	IV (25 lb.
Luperox ANS55 Luperox ANS55P	Dibenzoyl Peroxide Dibenzoyl Peroxide	Paste Mixture Paste Mixture	BBP & filler BBP & Filler	25% 25%	38° C/100° F	54° C (50# ctn) 54° C (50# ctn)		77	77	IV (350 lb.) IV (350 lb.)
Luperox AFR40	Dibenzoyl Peroxide	Paste Misture	DBP & Calcium STEARATE	40%	38° C/100° F	55° C (40# CTN)	-	2	2	IV (380 lb.)
ATOEO ATOEO	Objection Deposited	Docto Misture	Tricresyl	700	7 000 70 00	NIT NIT	. 5	, <u>}</u>	1 1/2	L
Luperox ATC30	Diberzoyi Peroxide	Paste Mixiure	Pricelcium	20%	38 C/100 F	NE	J.	IJ.	N.	뷜
Luperox ACP35	Dibenzoyl Peroxide	Paste Mixture	Phosphate	35%	38° C/100° F	NE	1	0	0	V (100 lb.)
Luperox P	t-Butyl Perbenzoate	Liquid Mixture	NA	%86	38° C/100° F	63° C (40# ctn)	1	3	3	II (5 gal.)
Luperox PAR70	t-Butyl Perbenzoate	Liquid Mixture	Aromatic 100	%02	38° C/100° F	est 63° C (40# ctn)	NE.	뮐	빙	E S
Luperox 7M75	t-Butyl peroxyacetate	Liquid Mixture	SMO	75%	38° C/100° F	79° C (7#ctn)	- <u>-</u>	m ½	m ½	l (5 gal.)
Luperox /iviso	1-bulyl peroxyacetate 2,4 Pentanedione	Fidula Mixiure	SMIO	50% 4% Active	38° C/100° F	85 C (/#CIII)	¥.	IJ.	N.	AN .
Luperox 224	Peroxide	Liquid	NA	Oxygen	(prefer<85°F)	54°C(42#ctn)	2	-	-	(V 5 gal. lb.)
Luperox DDM-9 (red)	Methyl Ethyl Ketone Peroxide	Liquid Mixture	Plasticizer	9% Active Oxygen	38° C/100° F	75° C (45# ctn)	3	2	2	IV (5 gal.) for DMP pro
Luperox DDM-30 (red)	Methyl Ethyl Ketone Peroxide	Liquid Mixture	Plasticizer	5.5% Active Oxygen	38° C/100° F	>85° C (8#ctn)	က	2	2	IV (5 gal.) for DMP pro
Linerax DHD-9 (red)	Methyl Ethyl Ketone Peroxide	I jamid Mixture	Plasticizer	9% Active	38° C/100° F	85° C (8#ctn)	85	2	2	IV (5 gal) for DMP pro
Linperox Delta X-9 (red)	Methyl Ethyl Ketone Peroxide	Liquid Mixture	Plasticizer	9% Active	38° C/100° F	85° C (8#ctn)		2	2	IV (5 gal.)
Clear Catalyst 11*	MEKP & Cumene Hydroperoxide	Liauid Mixture	Plasticizer	8.6% Active Oxygen (min)	38° C/100° F	NE	a W	ı W	ı W	N N
Red Catalyst 11*	MEKP & Cumene Hydroperoxide	Liauid Mixture	Plasticizer	8.6% Active Oxygen (min)	38° C/100° F	N	NE.	W.	NE	Z
Catalyst 730*	MEKP & Cumene Hydroperoxide	Liquid Mixture	Placticizer	8.7% Active	38° C/100° E	. AN	! <u>"</u>	! <u>"</u>	. 4	별
Luperox CU90	Cumene Hydroperoxide	Liquid	N	88 to 90%	38° C/100° F	82° C (5 gal. ctn)	<u>ب</u>	2	2	III (55 gal.)
Luperox TAEC	t-amyl peroxy-2- ethylhexyl carbonate	Liguid	AN	91%	38° C/100° F (prefer <85° F)	65° C (35#ctn)	N.	N.	N.	N
Luperox TBEC	t-butyl peroxy-2- ethylhexyl carbonate	Liquid	NA	65%	38° C/100° F (prefer <85° F)	65°C(35#ctn)	-	m	2	III (5 gal.)
Luperox TBIC M75	t-butylperoxy isopropyl carbonate	Liquid Mixture	OMS	75%	38° C/100° F (prefer <85° F)	65° C (35#ctn)	-	m	т	II (5 gal.)
Luperox DI	Di-t-butyl Peroxide	Liquid	NA	%86<	38° C/100° F	80° C (30#ctn)	1	3	2	III (55 gal.)
Luperox TBH 70X	t-butyl Hydroperoxide	Liquid Mixture	Water	70%	38° C/100° F	est. 88° C [35# ctn.]	3	2	2	IV (55 gal.)
Luperox TBH 70	t-butyl Hydroperoxide	Liquid Mixture	DTBP	70%	38° C/100° F	est. 88° C [35# ctn.]	3	3	3	II (55 gal.)
Luperox 555M60	t-amyl peroxyacetate	Liquid Mixture	OMS	%09	38° C/100° F	75° C [35# ctn.]	2	3	2	III(5 gal.)
Luperox TAP	t-amyl peroxybenzoate	Liquid	NA	62%	38° C/100° F	65° C [40# ctn.]	2	3	2	II(5 gal.)
Luperox DTA	Di-t-amyl Peroxide	Liquid	NA	%96	38° C/100° F	75° C [30# ctn.]	NE	NE	NE	NE
Luperox 130	2,5-Dimethyl 2,5 -Di (t-butylperoxy) hexyne-3	Liquid	NA	90 to 95%	38° C/100° F	93° C [35# ctn.]	NE	NE	NE	R
Luperox 130XL45	2,5-Dimethyl 2,5-Di (t-butylperoxy) hexyne-3	Solid Mixture	Calcium Carbonate	45%	38° C/100° F	88° C [100# ctn.]	NE	NE	P	핃
Luperox 101	2,5-Dimethyl 2,5 -Di (t-butylperoxy) hexane	Liquid	NA	91 to 93%	38° C/100° F	86° C [30# ctn.]	2	3	2	III (30 gal.)

V (100 lb.)	NE	NE	III (100 lb.)	V(100 lb.)	V(100 lb.)	V(100 lb.)	NE	IV(55 gal.)	V(100 lb.)	V(100 lb.)	V(100 lb.)	NE	III(5 gal.)	III(5 gal.)	II(5 gal.)	II(5 gal.)	V(100 lb.)	NE	II (5 gal.)	III(5 gal.)	II(5 gal.
1	NE	NE	2	0	0	0	NE	2	_	_	-	NE	2	2	3	3	1	NE	2	2	т
-	NE	NE	2	1	-	1	NE	2	-	-	-	NE	ж	3	က	က	<u></u>	NE	33	2	ю
-	NE	JE	1	_	-	1	NE	2	-	-	-	W	2	-	2	2	1	NE	2	2	F-
82° C [100# ctn.]	est. 82° C [100# ctn.]	est. 82° C [100# ctn.]	NE	NE	NE	NE	NE	91° C [40# ctn.]	NE	NE	NE	NE	60° C [30# ctn.]	80° C [35# ctn.]	66° C [35# ctn.]	est. 66° C [35# ctn.]	60° C [100# ctn.]	60° C [20# ctn.]	75° C [40# ctn.]	80° C [35# ctn.]	NE 65° C [35# cnt] for phthalate blend
38° C /100° F	38° C /100° F	38° C /100° F	38° C /100° F	38° C /100° F	38° C /100° F	38° C /100° F	38° C /100° F	38° C /100° F	38° C /100° F	38° C /100° F	38° C /100° F	38° C /100° F	32° C /90° F	32° C /90° F	32° C /90° F	32 °C /90° F	32° C /90° F	38° C /100° F	38° C /100° F	38° C /100° F	32° C /90° F
45%		20%	%/6	40%	40%	40%	40%	%66	40%	40%	40%	40%	80%	75%	92%	75%	40%	40%	95 - 98%	75%	80%
Calcium Carbonate	Mixture	Polypropylene	NA	Calcium Carbonate	Clay	Clay	EPM Rubber	NA	Calcium Carbonate	Clay	Clay	EPM Rubber	OMS	OMS	NA	Phthalate	Calcium Carbonate	Calcium Carbonate	NA	OMS	OMS
Solid Mixture	Solid Mixture	Solid Mixture	Liquid	Liquid	Solid	Solid	Solid	Solid	Solid	Solid	Solid	Solid	Liquid Mixture	Liquid	Liquid	Liquid	Solid	Solid	Liquid	Liquid	Liquid Mixture
2,5-Dimethyl 2,5 -Di (t-butylperoxy) hexane	2,5-Dimethyl 2,5-Di (t-butylperoxy) hexane	2,5-Dimethyl 2,5-Di (t-butylperoxy) hexane	Di-2-t-butylperoxy isopropyl benzene	Di-2-t-butylperoxy isopropyl benzene	Di-2-t-butylperoxy isopropyl benzene	Di-2-t-butylperoxy isopropyl benzene	Di-2-t-butylperoxy isopropyl benzene	Dicumyl Peroxide	Dicumyl Peroxide	Dicumyl Peroxide	Dicumyl Peroxide	Dicumyl Peroxide	1,1 Di(t-amylperoxy) cyclohexane	Ethyl 3,3 di- t-amyl peroxy butyrate	1,1 di-t-(butylperoxy 3,3,5 trimethyl cyclohexane	1,1 di-t-(butylperoxy 3,3,5 trimethyl cyclohexane	1,1 di-t-(butylperoxy 3,3,5 trimethyl cyclohexane	n-butyl 4,4 bis t-butyl peroxy valerate	n-butyl 4,4 bis t-butyl peroxy valerate	Ethyl 3,3 di- t-butyl peroxy butyrate	1,1 Di(t-butylperoxy) cyclohexane
Luperox® 101XL45	Luperox HP101 XLP	Luperox 101PP20	Luperox F	Luperox F40P	Luperox F40KE	Luperox F40KEP	Luperox F40MG	Luperox DCSC	Luperox DC40P	Luperox DC40KE	Luperox DC40KEP	Luperox DC40MG	Luperox 531M80	Luperox 533M75	Luperox 231	Luperox 231P75	Luperox 231XL40	Luperox 230XL40	Luperox 230	Luperox 233M75	Luperox 331M80

NOTE: Lupersol® DDM-9*, DDM-30*, DHD-9* and Delta X-9* trade names are scheduled to change to those indicated in the table during 2000 or 2001. PRODUCT FORMULATIONS WILL NOT CHANGE.

Table 3 Arkema Inc. Refrigerated Products

Trade Name	Peroxide Name	Physical Form	Diluent	Assay (%)	
Luperox SAP	succinic acid peroxide	Frozen Solid	Water	57.29	
Luperox 610M50	2-Hydroxy-1, 1-dimethyl butylperoxyneodecanoate	Liquid Mixture	OMS	50%	
Luperox 575	t-amyl peroxy -2-ethyl hexanoate	Liquid	NA	95%	
Luperox 575M75	t-amyl peroxy -2-ethyl hexanoate	Liquid Mixture	OMS	75%	
Luperox 11M75	t-butyl peroxypivalate	Liquid Mixture	OMS	75%	
Luperox 11M45	t-butyl peroxypivalate	Liquid Mixture	OMS	45%	
Luperox 10	t-butylperoxy neodecanoate	Liquid	NA	>99%	
Luperox 10M75	t-butylperoxy neodecanoate	Liquid Mixture	OMS	75%	
Luperox 221	di-n-propyl peroxydicarbonate	Liquid	NA	>99%	
Luperox 223S	di-2-ethylhexyl peroxydicarbonate	Liquid	NA	>97%	
Luperox 223M75S	di-2-ethylhexyl peroxydicarbonate	Liquid Mixture	OMS	75%	
Luperox 225S	di-sec-butyl peroxydicarbonate	Liquid	NA	>98%	
Luperox 225M60S	di-sec-butyl peroxydicarbonate	Liquid Mixture	OMS	60%	
Luperox 188M75	alpha-cumyl peroxy neoheptanoate	Liquid Mixture	OMS	75%	
Luperox 288M75	alpha-cumyl peroxy neoheptanoate	Liquid Mixture	OMS	75%	
Luperox 546M75	t-amyl peroxyneodecanoate	Liquid Mixture	OMS	75%	
Luperox 554M75	t-amyl peroxypivalate	Liquid Mixture	OMS	75%	
Luperox 554M50	t-amyl peroxypivalate	Liquid Mixture	OMS	50%	
Luperox 256	2,5 dimethyl 2,5 bis-2- ethyl hexanoyl peroxy hexane	Liquid	NA	>90%	
Luperox DEC	Didecanoyl peroxide	Solid	NA	>98.5%	
Luperox 26	t-butyl peroxy 2-ethyl hexanoate	Liquid	NA	>97%	
Luperox 26M50	t-butyl peroxy 2-ethyl hexanoate	Liquid Mixture	OMS	50%	
Luperox 26P50	t-butyl peroxy 2-ethyl hexanoate	Liquid Mixture	Phthalate	50%	
Luperox M33	1,1 Di(t-butylperoxy) cyclohexane & t-butyl peroxy-2-ethylhexanoate	Liquid Mixture	OMS	65%	

 $[\]dagger$ Data referenced from NFPA 432 Code for the storage of organic peroxide formulations; 1997 edition.

OMS – odorless mineral spirits

SADT – Self Accelerating Decompostion Temperature

Note: Lupersol® DDM-9*, DDM-30*, DHD-9* and Delta X-9* trade names are scheduled to change to those indicated in the table during 2001. PRODUCT FORMULATIONS WILL NOT CHANGE.

REMARKS

Luperox 223 M75S Possible phase separation below 0°F (–18°C). (C)

Luperox 11 M75 Freezes at -2°F (-19°C). Thawing at storage temperature returns to

storage temperature returns to original form.

NOTES:

Rapid decomposition gives gasses which may spontaneously ignite in air.

Phase separation and crystallization of solutions - to return homogenous solution, let stand at recommended storage temperature, with occasional mixing or shaking.

Max. Storage Temp °F (C°)	SADT	NFPA Code 704 Health Hazard ID.†	NFPA Code 704 Flamm. Hazard ID.†	NFPA Code Reactivity Hazard ID.†	NFPA Code 432 Storage Class†
32 ° F [0° C]	66° C [1# bag]	NE	NE	NE	NE
0° F [-18° C]	25° C [7# ctn]	NE	NE	NE	NE
50° F [10° C]	45° C [35# ctn]	0	3	2	III (55 gal.)
50° F [10° C]	45° C [35# ctn]	NE	NE	NE	NE
32° F [0° C] NOT <0° F (-18° C)	29° C [35# ctn]	2	3	3	II (5 gal.)
32° F [0° C] NOT <0° F (-18° C)	45° C [30# ctn]	NE	NE	NE	NE
14° F [-10° C]	21° C [30# ctn]	NE	NE	NE	NE
14° F [-10° C]	27° C [35# ctn]	2	3	2	III (5 gal.)
-10° F [-23° C]	-7° C [9# ctn]	2	3	4	l (1 gal.)
0° F [-18° C]	15° C [8# ctn]	1	3	3	II (1 gal.)
14° F [-10° C]	20° C [7# ctn]	NE	NE	NE	NE
14° F [-10° C]	10° C [8# ctn]	1	3	3	II (1 gal.)
14° F [-10° C]	15° C [35# ctn]	NE	NE	NE	NE
5° F [-15° C]	15° C [37# ctn]	1	3	2	III (5 gal.)
0° F [-18° C]	20° C [35# ctn]	2	3	2	III (5 gal.)
14° F [-10° C]	25° C [30# ctn]	1	3	2	III (5 gal.)
20° F [-7° C]	30° C [30# ctn]	1	3	2	III (5 gal.)
20° F [-7° C]	NE	NE	NE	NE	NE
60° F [16° C]	40° C [35# ctn]	0	3	2	III (5 gal.)
60° F [16° C]	43° C [50# ctn]	1	3	2	III (50 lb.)
50° F [10° C]	42° C [35# ctn]	1	3	2	III (5 gal.)
60° F [16° C]	54° C [30# ctn]	1	2	2	III (55 gal.) IV (5 gal.)
60° F [16° C]	65° C [7# ctn]	1	2	2	III (55 gal.) IV (5 gal.)
15°C/59° F	NE 65°C [35# cnt] for phthalate blend	NE	NE	NE	NE NE

HAZARD OVERVIEW BY PEROXIDE FAMILY

Included below is information about specific product classes, i.e., salient points about certain organic peroxides in these groups as they relate to these hazards as discussed in section 3.

PEROXIDE CLASSES

A. DIACYL PEROXIDES

Dry benzoyl peroxide (Luperox® A98) is shock and friction sensitive. Except for Luperox A98, commercial diacyl peroxides are formulated to be non-shock or non-friction sensitive and must be handled and stored properly. Examples include the wetted and paste forms of benzoyl peroxide. Wet forms of benzoyl peroxide should not be allowed to dry out.

B. PEROXYESTERS

Peroxyesters are quite stable at their recommended storage temperatures. The recommended temperatures for those materials requiring refrigerated storage should be strictly adhered to (consult Arkema Inc.'s Peroxyesters Product Bulletin).

Some peroxyesters (such as Luperox P) can freeze. Frozen materials can be thawed by placing in storage at recommended temperature.

C.PEROXYDICARBONATES

Peroxydicarbonates are thermally unstable compounds. At their recommended storage temperatures however they are not expected to decompose. Above the recommended storage temperatures, decomposition will occur, and in some cases violent decomposition.

D.DIALKYL PEROXIDES

Most Dialkyl peroxides have relatively high flash points, but once ignited, will burn vigorously and are difficult to extinguish. However, Di-t-Butyl Peroxide and Di-t-Amyl Peroxide have a low flash point and their vapors are highly flammable; thus, they must be handled as a flammable liquid as well as an organic peroxide. Specific handling and use information are available upon request from Arkema Inc.

E. KETONE PEROXIDES

Ketone peroxides are corrosive to eyes and irritants to skin. As a group, the ketone peroxides are subject to decomposition through chemical action and are particularly sensitive to metallic salts. They are widely used as room temperature catalysts for curing polyester resins which contain accelerators such as cobalt naphthenate and cobalt/tertiary amine combinations.

Direct mixtures of the peroxide and the accelerator may decompose with violence and every effort should be made to eliminate any possibility of direct contact. Because of the wide range of contaminants which can interact with ketone peroxides, good housekeeping practices should be strictly maintained. Methyl Ethyl Peroxides should never be diluted with Acetone.

F. PEROXYKETALS

Peroxyketals are extremely sensitive to acid contamination which causes rapid decomposition releasing flammable vapors which may self ignite.

G.HYDROPEROXIDES

Hydroperoxides are generally corrosive to skin and eyes. Commercial formulations of Hydroperoxides as supplied by Arkema Inc. are not shock sensitive. Pure t-butyl hydroperoxide and 2,5-dihyroperoxy-2,5-dimethyl hexane are considered too shock sensitive for commercial handling. Hydroperoxides, in particular cumene hydroperoxide, (Luperox CU90) are sensitive to contamination. Contact with incompatible materials (such as strong acids and strong oxidizers) can lead to a violent decomposition.

STORAGE

In general, one of the most important factors to observe when working with organic peroxides is the required storage temperature. Exposure to a temperature that can lead to an accelerated decomposition may result in the generation of flammable gasses and, in some cases, spontaneous ignition. Proper storage is critical to the safe handling of organic peroxides. particularly those requiring controlled temperature storage. Ventilation is important because air circulation around peroxides stored at low temperatures reduces the chance of localized hot spots that can cause decomposition.

Organic peroxide inventory should be rotated to avoid shelf life problems. Only minimal quantities of peroxide should be kept in the immediate processing area. Freezer or refrigerated facilities should be provided for intermediate storage of controlled temperature products.

Note: It should be kept in mind that refrigerated storage facilities are used to maintain low temperature peroxides at the required storage temperature and not for cooling low temperature peroxides to the required temperature. Although NOT recommended by Arkema Inc., if only a portion of material that is removed from refrigerated storage is used, the remainder must be cooled to a temperature at, or somewhat below, the required temperature before being placed back into the refrigerated storage facilities. Failure to follow this procedure could result in a serious decomposition in the refrigerated storage area.

Basic Guidelines

All peroxide storage facilities should be designed along the following basic guidelines:

- Comply with Federal, State and Local requirements. Consult NFPA 432 for organic peroxide storage guidelines.
- 2. Located in an isolated area.
- 3. Used only for the storage of organic peroxides.
- 4. Should be of fireproof construction.
- 5. Electrical equipment should be explosion proof:
 - Storage Areas = Class I Division II Group D
 - Process Areas = Class I Division I Group D
- 6. Free of all combustible material.
- 7. Prevent exposure to sunlight.
- 8. Posted signs "Organic Peroxide Storage" and "No Smoking".
- For controlled temperature peroxides, emergency back up refrigeration should be installed.
- For controlled temperature peroxides, emergency sources of dry ice should be locally available.

Large quantities of organic peroxides should ideally be stored in specially designed buildings of noncombustible construction. Detached buildings are the most common and preferred facilities for storing large quantities. Three basic

types of buildings are used depending on the storage requirement of the peroxide and the amount that will be stored, plus local fire codes, insurance regulations and other laws.

A.Uncontrolled Temperature Storage

Products stored in this type of building do not normally require storage temperatures outside of the normal ambient range (100°F max.) to maintain assay, prevent self accelerating decomposition and freezing. Uncontrolled temperature storage however should not exceed 100°F. Depending on climate, buildings can be insulated, ventilated and/or double walled. (See Figure 2)

B. Refrigerated Storage Facilities

Products stored in this type of facility require lower than normal ambient temperatures to preserve assay and to prevent self accelerating decomposition, e.g. chest type freezers.

C.Walk In Refrigerated Storage Building

This type of facility is suitable for storing large quantities of peroxide which require refrigerated conditions, e.g. Peroxydicarbonates. (See Figure 3)

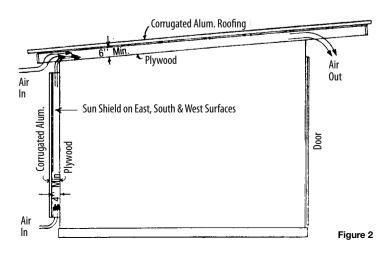


Figure 3 Walk-In Type Storage Unit Refrigerated storage building and key requirements, inside and out. Organic Peroxide Diamond on each exterior wall. Safety release door opens with pressure. "Flammable Storage-Keep Fire Away" and "No Smoking" placards on outside of building. Temperature recorder and temperature alarm system (visual and audio). Metal portions of building should be grounded. Explosion-proof electrical equipment (Outside and Inside). Refrigeration units; Main and emergency backup systems (fluorocarbon type), located outside or away from building. For low-temperature peroxide storage (i.e. Lupersol® 223S, Luperox® 10M75) a liquid nitrogen fire protection system is recommended. Interior and exterior walls should be made of corrosion resistant design. Minimum insulation should be 3 inches of urethane for walls, ceiling and floor. Weather-proof covering and sun-shield over top of building. Inside evaporators; Main and emergency backup systems. Corrugated fiberglass on walls, pallets on floor, and spacing between rows of cartons; for air circulation.

SPILLAGE AND DISPOSAL

Organic peroxide spills must be taken care of immediately. Spills can normally be handled by spreading an inert absorbent material directly on the spill, sweeping the area and placing the sweepings in polyethylene bags for disposal. The sweepings should be wetted down with water and disposed of immediately by an approved disposal method (see below). When all the material has been picked up, wash down the spill area with surfactant and water to remove any traces of peroxide. Allow for sufficient ventilation to aid in the removal of fumes that may be present.

The following is the recommended method for disposal of organic peroxides.

DILUTION AND INCINERATION

Due to current environmental regulations, this method is quickly becoming the most preferred for liquid peroxide disposal. Dilution of peroxide to no

more than 1% active oxygen, or no more than 10% by weight (whichever is lower) in a satisfactory solvent is recommended. Fuel Oil #2 or non-flammable-polymerizable hydrocarbons (which are readily soluble with the peroxide) are the most widely used solvents. Incineration can be accomplished after satisfactory mixing. Incineration has the advantage of providing rapid and complete decomposition along with the elimination of decomposition products. This method is not generally recommended for disposal of solid peroxides due to limited solubility of solid peroxides with hydrocarbons.

Incineration must be performed in accordance with all applicable Federal, State and Local regulations. In general, an outside disposal company is used to perform this service.



PACKAGING

The containers in which organic peroxides are packaged include polyethylene bottles and jars, polyethylene lined bags and fiber drums and specially coated steel drums. Polyethylene is the preferred material since it is relatively inert and is flexible enough to withstand normal pressure buildup. Examples of typical containers are shown below.



TRANSPORTATION

Transportation regulations for organic peroxide formulations are located in the Code of Federal Regulations (CFR); 49 CFR 173.225.

Certain peroxides require refrigerated transportation as specified in 49 CFR 173.21(f)(3).



FIRST AID

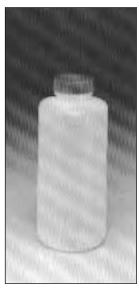
Care should be exercised by all personnel handling organic peroxides. Acute hazards of organic peroxides may include skin/eye irritation, skin/eye corrositivity, and skin sensitization. Refer to MSDS or label for specific product health effects and first aid information.

For immediate medical assistance contact the Rocky Mountain Poison Control Center at 303-623-5716.









SAFETY CHECK LIST

The following check list is provided as a summary in an attempt to avoid problems in the storage, handling or use of organic peroxides. The list is a basic safety and information guide, as it pertains to all organic peroxides.

- 1. Different classes of organic peroxides have their own particular characteristics, specifications and handling requirements. These are identified on the product labels and described in the appropriate product bulletins and MSDS. The product label is designed to indicate recommended storage temperature, specific product hazard characteristics, special handling information and appropriate first aid instructions. Product bulletins provide chemical composition data, sales specifications (including shelf life), physical properties, and safety information, such as storage temperature and SADT (Tables 2 and 3).
- 2. One of the most important factors to observe when working with an organic peroxide is the recommended storage temperature. Exposure to a temperature that can lead to an accelerated decomposition may result in the generation of flammable gasses, and in some cases spontaneous ignition.
- **3.** Refer to NFPA 432 for storage guidelines. Proper storage is critical to the safe handling of organic peroxides, both those normally stored at ambient temperatures and those requiring controlled temperature storage. Ventilation is important because air circulation around peroxides stored at low temperatures reduces the chance of localized hot spots that could cause decomposition.
- **4.** Storage areas for peroxides should have explosion proof electrical equipment.
- **5.** Organic peroxide inventories should be rotated to avoid shelf life problems.
- **6.** Any observable gassing or distortion of the container, should be treated very carefully. Visible gassing of

- organic peroxide containers may be an indication of imminent, possibly violent decomposition.
- **7.** Only minimal quantities of peroxides should be kept in the immediate processing area.
- **8.** Avoid contact with incompatible materials, such as oxidizers, reducing agents, promoters, acids or bases.
- **9.** The safe use of organic peroxides demands that good housekeeping procedures be meticulously practiced.
- **10.** Heat, flame, contamination, shock, friction and static electricity are potential hazards when an organic peroxide is being charged to a reaction. Care should be taken to eliminate or minimize all of these.
- 11. Contamination can be avoided by using proper equipment and proper materials of construction. Polymeric materials that may be soluble in organic peroxide solutions should not be used as reaction vessels. Compatible materials of construction include stainless steel 304 or 316 (preferred), HDPE, polytetrafluorothylene and glass linings. Do not use copper, brass or iron.
- **12.** Foreign materials, such as iron or dirt, should be avoided when charging peroxides.
- **13.** Pumps used for organic peroxides must be "dedicated use" to avoid potential contamination.
- **14.** Static buildup can be minimized by proper grounding and by keeping free fall distances to a minimum, especially when working with static sensitive initiators, such as dry benzoyl peroxide, and di-t-butyl peroxide.
- **15.** Friction caused by pumping increases the temperature of the pumped solutions. Extra care should be exercised when peroxide solutions are being re-circulated to avoid temperatures above SADT.
- **16.** When peroxide samples are used in analytical work, care should be exer-

- cised to avoid any contamination. Clean, dry plastic or glass containers should be used to transfer peroxide samples. Dry ice should be available to cool samples in an emergency. Direct heat should never be applied to organic peroxides.
- **17.** As a rule, dilution of pure peroxides with compatible solvents will increase the safety characteristics of the peroxides.
- **18.** Any spilled organic peroxides should be attended to immediately. Spills can normally be handled by spreading an inert absorbent substance directly on the spill, wetting with water, sweeping the area and then placing the sweepings in polyethylene bags for appropriate disposal.
- **19.** Where spills occur, allow for sufficient ventilation to aid in the removal of fumes that may be present.
- **20.** In disposing of organic peroxides, or the absorbent material that has been used to remove spills, extreme care should be exercised. The wetted absorbent material should be placed in a plastic bag and then incinerated. Federal, State and Local laws and environmental regulations must be observed in choosing a disposal method.
- 21. The procedure for disposal of empty peroxide containers must include a thorough draining and should include rinsing with water or a compatible solvent in particular for refrigerated products. In accordance with Federal, State and local regulation, these can then be sent to an approved disposal site or incineration site.
- **22.** Drum containers must always be thoroughly flushed and drained before being sent to a reconditioner.
- **23.** Cutting torches should never be used on empty peroxide drums. Flammable vapors may be present.

CONCLUSION

A thorough understanding of the safety characteristics of organic peroxides is necessary in order to prevent accidents and to permit safe operations. The recommendations made in this Bulletin are presented as a service to aid in the safe handling, storage and disposal of organic peroxides. The safety tests described herein were used to establish safe handling procedures, packaging and shipping procedures for all organic peroxides. These guidelines are suggested to aid users of organic peroxide initiators.

Available Safety Films

1. "Handle With Care"

Discusses the hazards of peroxides storage and handling and offers recommended procedures.

2. "Keep It Cool and Keep It Clean"

Considers hazards and preventative measures relative to MEK peroxide use in unsaturated polyester applications.

Other Information Sources

- National Fire Protection Association (NFPA) www.nfpa.org
 1-800-344-3555
 NFPA 432 Code for the Storage of Organic Peroxide Formulations.
- The Society of The Plastics Industry, Inc. (SPI)
 Organic Peroxide Producers Safety Division (OPPSD)
 www.plasticsindustry.org
 1-202-974-5200

Safety and Handling of Organic Peroxides: A Guide (Publication #AS-109)

Responsible Care

Arkema Inc. is committed to the ACC's Responsible Care® and Product Stewardship initiatives.

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SAFE USE AND HANDLING OF AMBIENT ORGANIC PEROXIDE INITIATORS

- 1. Know the storage temperature and do not exceed it.
- 2. Know the **SADT** "Danger Temperature" and respect it.
- 3. Leave room for cool air circulation in storage area; follow the 2 foot rule.
- 4. Equip storage area properly.
- 5. Have fire extinguishers available.
- 6. Rotate inventory: "First In, First Out".
- 7. Take only the amount that will be used.
- 8. Do NOT return unused initiator to storage buildings.
- 9. Rinse and slash containers prior to disposal.
- 10. Immediately clean up spills and dispose of them properly.
- 11. Protect your eyes and skin.
- 12. Use appropriate Personal Protective Equipment (PPE).
- 13. Initiator in large vessels should be diluted.
- 14. Know your plant's emergency procedures.

Above all, when it comes to storing, handling and using organic peroxide initiators, "Don't Lose Your Cool!"

For additional information consult the Material Safety Data Sheet (MSDS).



Arkema Inc. • Fine Chemicals Group • Organic Peroxides
2000 Market Street, Philadelphia, PA 90103
Phones: (800) 558-5575 • Fax: (215) 419-7413 • 24-Hour Emergency (800) 424-9300
www.Arkema-Inc.com



Arkema Inc. is committed to the ACC's Responsible Care and Product Stewardship initiatives.

In Case of Emergency Call CHEMTREC at 1-800-424-9300

For Medical Assistance Call R.M.P.C.C. at 1-303-623-5716



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