

ORGANIC PEROXIDES

Product Bulletin

Peroxide Selection Guide for Molding Unsaturated Polyester Resins at *Elevated Temperatures*

INTRODUCTION

This bulletin is designed to aid in the selection of optimum peroxide initiator systems for elevated temperature molding processes. To provide the molder with the choice and flexibility needed to meet the most exacting performance requirements, ATOFINA Chemicals maintains the most extensive product line available, and provides specialized customer service as well.

PEROXIDE DECOMPOSITION

Organic peroxides have the general structure R-O-O-R'. Commercial peroxides used for elevated temperature molding are commonly categorized by their chemical structure, e.g., the five types or classes shown in Table 1.

The thermal decomposition of peroxides in polyester resins initially involves cleavage of the -O-O- bond to give two free radicals RO• and R'O•. These high energy fragments may then react with monomer to initiate the desired polyester cross-linking reaction. The radicals may also form decomposition products and other free radicals by abstracting hydrogen from solvent, monomer or polymer. The exothermic crosslinking reaction converts the liquid resin into a three-dimensional, hard, thermoset solid.

TABLE 1
Commercial Initiator Classification

Type	Structure	10-Hr. T _{1/2} Range, °C
A Diacyl peroxide	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{RC}-\text{OO}-\text{CR} \end{array}$	20 to 75
B Dialkyl peroxydicarbonate	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{ROC}-\text{OO}-\text{COR} \end{array}$	49 to 51
C tert-Alkyl Peroxyester	$\begin{array}{c} \text{O} \\ \parallel \\ \text{RC}-\text{OO}-\text{R}' \end{array}$	49 to 107
D Di-(tert-alkyl) Peroxyketal	$\begin{array}{c} \text{ROO} \quad \text{R}' \\ \diagdown \quad / \\ \text{C} \\ / \quad \diagdown \\ \text{ROO} \quad \text{R}' \end{array}$	92 to 115
E Di-tert-alkyl peroxide	R-OO-R'	117 to 133

PEROXIDE HALF-LIFE

A convenient way of expressing the decomposition rate of a peroxide at a specified temperature is in terms of its half-life i.e., the time required to decompose one-half of the peroxide originally present. To compare reactivity of different peroxides, the temperature at which each peroxide has a half-life (T_{1/2}) of 10 hours is used. At any given molding temperature the most reactive (fastest) peroxide would be the one with the lowest 10 hour T_{1/2} temperature.

PEROXIDE SELECTION GUIDELINES

Selection of the most cost-effective initiator for a specific molding process is based on the following primary factors:

1. Pot-life of the resin/peroxide mix
2. Molding temperature desired or as dictated by the process.

Each of these factors is highly dependent on the thermal sensitivity or half-life of the organic peroxides.

POT-LIFE—The first approach in choosing a peroxide is to select from those having the half-life characteristics which will provide the pot-life required by the process. As a general rule, molding formulations with pot-life requirements of several hours to one week (e.g. pultrusion) can use peroxides with 10 hour half-life temperatures of 80°C or less (Table 2), while those requiring pot-lives greater than one week (e.g. SMC, BMC) must employ peroxides with 10 hour half-life temperatures greater than 80°C (Table 3).

One class of peroxide, peroxyketals, provides much longer pot-lives than their half-life data indicate. Peroxyketals should be considered whenever faster mold cycle time (vs. t-butyl perbenzoate) and longer pot-lives are required, e.g., for sheet molding compound.

Naturally, other factors such as peroxide concentration, ambient temperature and formula additives will effect the actual pot-life of a given resin system.

Once peroxides have been selected which will provide the necessary pot-life, one must next consider the process mold temperature requirements.

MOLD TEMPERATURE—Generally the efficiency of an organic peroxide initiator depends on its thermal decomposition rate at a given mold temperature and on the ability of the free radicals formed to carry out the desired crosslinking reaction. As a general rule of thumb, a molding temperature is chosen that is approximately 40°C higher than the peroxide's 10 hour half-life temperature, Tables 2 and 3 list molding temperature ranges which provide a rough guide for specific peroxide selection. Molding at temperatures significantly greater than the optimum range is not recommended since radicals are generated too rapidly, resulting in inefficient use of the peroxide. This may result in undesirable side reactions such as polymer degradation. When molding temperatures fall below the optimum range, slow cure times are generally the rule (See Figure 2).

While half-life characteristics, pot-life and mold temperature are major factors in selecting a peroxide, they are not the only consideration for a particular molding application. Other factors include: thickness of the molded

part, effect of filler and other additives, cost, safety, necessity for refrigerated storage and shipment, effect on final product and need for activation. Where questions exist, contact an ATOFINA Chemicals representative for advice and recommendations.

COMMERCIAL PEROXIDES

Peroxide initiators are listed in Tables 2 and 3 in order of increasing 10 hour half-life temperatures. To aid in the selection process, the approximate molding temperature range and pot-life are shown along with the maximum recommended storage temperature. In general, peroxides which provide the fastest molding cycles will usually reduce the pot-life of the resin formulation. **Some of these initiators require refrigerated storage.** Blends of stable high temperature initiators and more reactive low temperature initiators are often used to achieve the best balance between cure time and pot-life of the resin formulation.

TABLE 2
INITIATORS FOR MOLDING AT 65°C TO 135°C (149°F TO 275°F)

INTRODUCTION							
This table lists "fast" initiators which are often used at low to moderately elevated molding temperatures in the range of 65° to 135°C. Molding formulations which utilize these initiators generally have short pot-lives;				from several hours to 7-10 days. These initiators are used in processes such as pultrusion, filament winding and resin transfer molding, as well as in initiator blends for molding at higher temperatures.			
Trade Name	Chemical Name	Chemical ⁽¹⁾ Type	10 Hr T _{1/2} Temp (°C)	Max. Storage Temp		Typical Molding Temp Range °C (°F)	Typical ⁽²⁾ Pot-Life (Days)
				°C	°F		
Luperox 188M75	-cumyl peroxyneodecanoate	C	38	-18	0	65-95 (150-205)	0.5-1
Luperox 288M75	-cumyl peroxyneopheptanoate	C	43	-18	0	65-95 (150-205)	0.5-1
Luperox 546M75	t-amyl peroxyneodecanoate	C	46	-10	14	70-100 (160-210)	0.5-1
Luperox10M75	t-butyl peroxyneodecanoate	C	48	-10	14	70-100 (160-210)	0.5-1
Luperox 223-M75S	di-(2-ethylhexyl) peroxy-dicarbonate	B	49	-10	14	75-105 (170-220)	0.5-1
Luperox 554M75	t-amyl peroxy-pivalate	C	55	-7	20	80-110 (715-230)	1-3
Luperox 11M75	t-butyl peroxy-pivalate	C	58	0	32	80-110 (175-230)	1-3
Luperox 256	2,5-dimethyl-2,5 bis(2-ethyl-hexanoylperoxy)hexane	C	73	10	50	100-130 (210-265)	3-7
Luperox AFR40	dibenzoyl peroxide	A	73	38	100	100-130 (210-265)	4-10
Luperox 575M75	t-amyl peroxy-2-ethylhexanoate	C	75	10	50	100-130 (210-265)	8-12
Luperox 26 ⁽³⁾	t-butyl peroxy-2-ethylhexanoate	C	77	10	50	105-135 (220-275)	8-12

(1) A = Diacyl B = Peroxydicarbonate, C = Peroxyester

(2) Pot-Life determined in 100g of net resin at 80°F

(3) Available pure and 50% active Luperox 26M50

Table 3
INITIATORS FOR MOLDING AT 120°C TO 170°C (250°F TO 340°F)

INTRODUCTION							
This table lists more stable initiators often used for molding at temperatures in the range of 120° to 170°C. Molding formulations which utilize these initiators generally				have long pot-lives; from several weeks to several months. Processes which utilize these initiators include bulk molding compounds (BMC) and sheet molding compounds (SMC).			
Trade Name	Chemical Name	Chemical Type ⁽¹⁾	10 Hr T _{1/2} Temp (°C)	Max. Storage Temp		Typical Molding Temp Range °C (°F)	Typical ⁽²⁾ Pot-Life (Days)
				°C	°F		
Luperox 531M80	1,1-di-(t-amylperoxy) cyclohexane	D	93	38	100	120-150(250-300)	60-90
Luperox 231P75	1,1-di-(t-butylperoxy) 3,3,5-trimethyl cyclohexane	D	96	38	100	120-150 (250-300)	60-90
Luperox 331M80	1,1-di-(t-butylperoxy) cyclohexane	D	97	32	90	120-150 (250-300)	60-90
Luperox TAEC	00-t-Amyl-0(2-ethylhexyl) monoperoxy carbonate	C	98	38	100	125-155 (260-310)	20-40
Luperox TBIC-M75	00-t-butyl 0-isopropyl monoperoxy carbonate	C	99	38	100	125-155 (260-310)	20-40
Luperox TBEC	00-t-butyl 0-(2-ethylhexyl) monoperoxy carbonate	C	100	38	100	125-155 (260-310)	20-40
Luperox TAP	t-amyl peroxybenzoate	C	100	38	100	125-155 (260-310)	30-45
Luperox 7M75	t-butyl peroxyacetate	C	102	38	100	125-155 (260-310)	30-45
Luperox P	t-butyl peroxybenzoate	C	104	38	100	130-160 (265-320)	30-45
Luperox 533M75	ethyl 3,3-di-(t-amylperoxy) butyrate	D	112	38	100	140-165 (285-330)	60-90
Luperox 233M75	ethyl 3,3-di-(t-butylperoxy) butyrate	D	114	38	100	140-165 (285-330)	60-90
Luperox DCSC ⁽³⁾	dicumyl peroxide	E	117	38	100	145-170 (295-340)	60-90

⁽¹⁾ C = Peroxyester D = Peroxyketal E = Dialkyl Peroxide

⁽²⁾ Pot-Life determined in 100g of neat resin at 80°F

⁽³⁾ Available also in technical grade and extended forms

PEROXIDE APPLICATION INFORMATION

Each type or class of peroxide (Table 1) has certain special characteristics which make them particularly useful in specific molding applications. A brief description of these is outlined below.

A. DIACYL PEROXIDES—Benzoyl peroxide (BPO) is the most popular diacyl peroxide for molding at 90-125°C (195-260°F). BPO is available in granular solid (Luperox A75 & A98), paste (Luperox ANS55), powder (Luperox ACP 35) and liquid suspension (Luperox AFR40) forms.

B. PEROXYDICARBONATES—Peroxydicarbonates (Lupersol 223-M75S) are affective at molding temperatures as low as 65°C (150°F) without the use of accelerators. They are often used in combination with a more stable peroxide such as t-butyl perbenzoate (Luperox P).

C. PEROXYESTERS—Peroxyesters offer the broadest 10 hour half-life temperature range and are useful at molding temperatures between 65°C (150°F) (Luperox 188M75, Luperox 10M75), and 160°C (320°F), (Luperox 7M75, Luperox P).

Peroxyesters can also be readily accelerated by transition metals such as cobalt or vanadium to decrease cure times at a given molding temperature.

D. PEROXYKETALS—Peroxyketals (Luperox 531M80, Luperox 331M80) offer fast cure reactivity combined with long pot-lives because they are resistant to induced decomposition caused by formulation components such as pigments and fillers.

E. DIALKYL PEROXIDES—Dialkyl peroxides are among the most stable of all commercially available peroxides. When they are used it is generally at temperatures above 105°C (300°F) (Luperox DCSC).

F. T-AMYL PEROXIDES—t-Amyl peroxides are more reactive than their t-butyl counterparts; therefore they offer faster mold turnover with only a minor sacrifice of pot-life. Additionally, t-amyl peroxides can reduce residual styrene levels. Overall, greater efficiencies yield savings in raw materials, mold cycle times and/or energy costs. (Luperox 575M75, Luperox 531M80, Luperox TAP).

G. BLENDS OF INITIATORS—Blends of more reactive initiators such as Luperox 26 and less reactive initiators such as Luperox 331M80 can often be utilized to produce dramatic reductions in cure times with only a slight decrease in resin pot-life. Such blends offer greater flexibility in the compromise pot-life and cure activity. (Luperox M33).

TYPICAL CURE PERFORMANCE

The rate at which any given polyester resin cures is directly dependent on two factors; peroxide concentration and cure temperature. These relationships are illustrated in Figures 1 and 2.

1. **PEROXIDE CONCENTRATION**—typically peroxide concentrations range from 0.5 to 2.0 parts by weight per one hundred parts of resin (phr). At lower concentrations, cures may be slow and physical property deterioration may be encountered. Higher peroxide concentrations are not cost effective since initiator is lost in wasteful side reactions.

The general relationship between peroxide concentration and cure time is shown for selected peroxides in figures 1A and 1B.

2. **CURE TEMPERATURE**—The general relationship between cure temperature and cure time is illustrated in Figure 2. Optimal molding temperature ranges for each initiator are highlighted.

FIGURE 1A
THE INFLUENCE OF PEROXIDE CONCENTRATION ON CURE TIME AT 82°C (180°F)

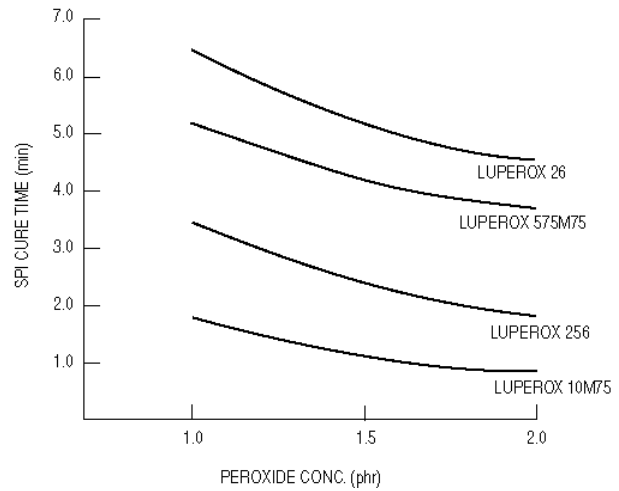


FIGURE 1B
THE INFLUENCE OF PEROXIDE CONCENTRATION ON CURE TIME AT 127°C (260°F)

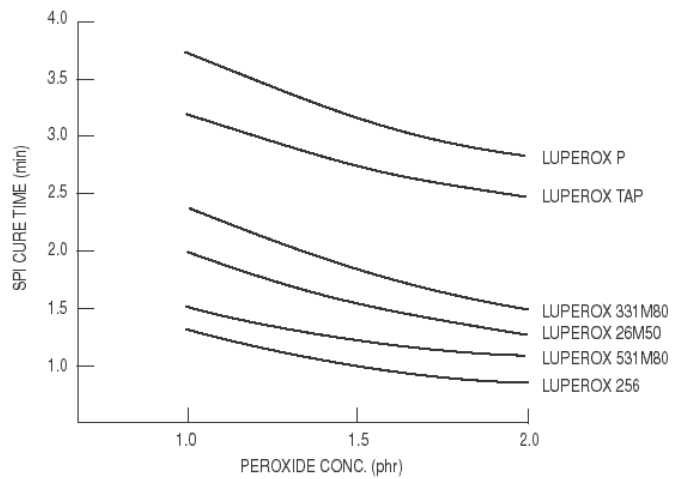
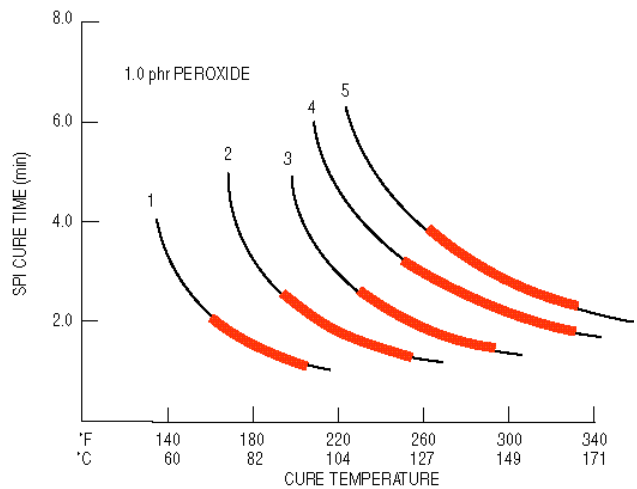


FIGURE 2
THE INFLUENCE OF TEMPERATURE ON RESIN CURE TIME



- | | |
|-------------------|-------------------|
| 1. LUPEROX 10M75 | 4. LUPEROX P |
| 2. LUPEROX 26 | 5. LUPEROX 233M75 |
| 3. LUPEROX 331M80 | |

GLOSSARY OF PEROXIDE TERMINOLOGY

ACTIVE OXYGEN—The extra atom in the peroxy compound (-O-O-) compared to its non-peroxy analog. Generally active oxygen is **measured** by analytical methods which involve the liberation of iodine from sodium iodide and the titration of liberated iodine with standard sodium thiosulfate solution. The **theoretical** active oxygen content can be calculated with the following formula:

$$\% \text{ A(O)} = \frac{(\text{number of available O-O}) \times 16 \times 100}{\text{molecular weight}}$$

ASSAY—The amount of a specific peroxide compound in a commercial formulation. Assay is a calculated value derived from the ratio of the **measured** active oxygen content to the **theoretical** active oxygen of the peroxide compound.

HALF-LIFE—The time it takes for one-half of a given quantity of peroxide in dilute solution to decompose at a given temperature. For example, t-butyl perbenzoate (Luperox P) has a half-life of 1.0 hr. at 125°C, 1.0 min. at 171°C and 1 second at 228°C. (Refer to HALFLIFE® Bulletin).

10 HOUR HALF-LIFE TEMPERATURE—The temperature at which the half-life of a peroxide is 10 hours. The 10 hour T½ temperature is a convenient bench mark to compare the relative stability and reactivity of different peroxides.

SADT (SELF-ACCELERATING DECOMPOSITION TEMPERATURE)—The temperature at which a peroxide, in its largest commercial package, will undergo self-accelerating decomposition. The SADT depends on the rate of decomposition, the heat loss from the package and the time at that temperature. This decomposition is usually rapid and may be violent (explosion, fire) depending on the degree of confinement and/or amount of available oxygen.

RECOMMENDED STORAGE TEMPERATURE—The temperature at which no significant peroxide decomposition, i.e., no loss in assay, will occur over a six month period.

POT-LIFE—the working life time (hours, days or weeks) of a resin formulation containing peroxide, Pot-life will vary depending on type and concentration of peroxide, filler type, inhibitor level and ambient temperature.

THERMOSET POLYMER—A crosslinked polymer that will not flow when heated, e.g., unsaturated polyester resin cured with organic peroxide initiator.

SAFETY CONSIDERATIONS

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

FLAMMABILITY

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

The flammability of organic peroxides is affected by the decomposition products; the decomposition generates vapors and heat. Such vapors may be flammable and depending on the degree of confinement, could result in an explosion.

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 decomposition will increase in an uncontrolled manner. This reaction can become violent, releasing large volumes of hot, flammable gasses.

The temperature at which this occurs depends on the volume of the peroxide, the container and the period of time the peroxide remains at the 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. (Refer to ATOFINA Chemicals' Bulletin "Safe Handling, Storage and Transportation of Peroxides Requiring Refrigeration").

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 and some alloys will have a similar effect over a longer period of time.

FURTHER INFORMATION

Consolidated Product Bulletins:

DIACYL PEROXIDES
PEROXYDICARBONATES
PEROXYESTERS
PEROXYKETALS
DIALKYL PEROXIDES

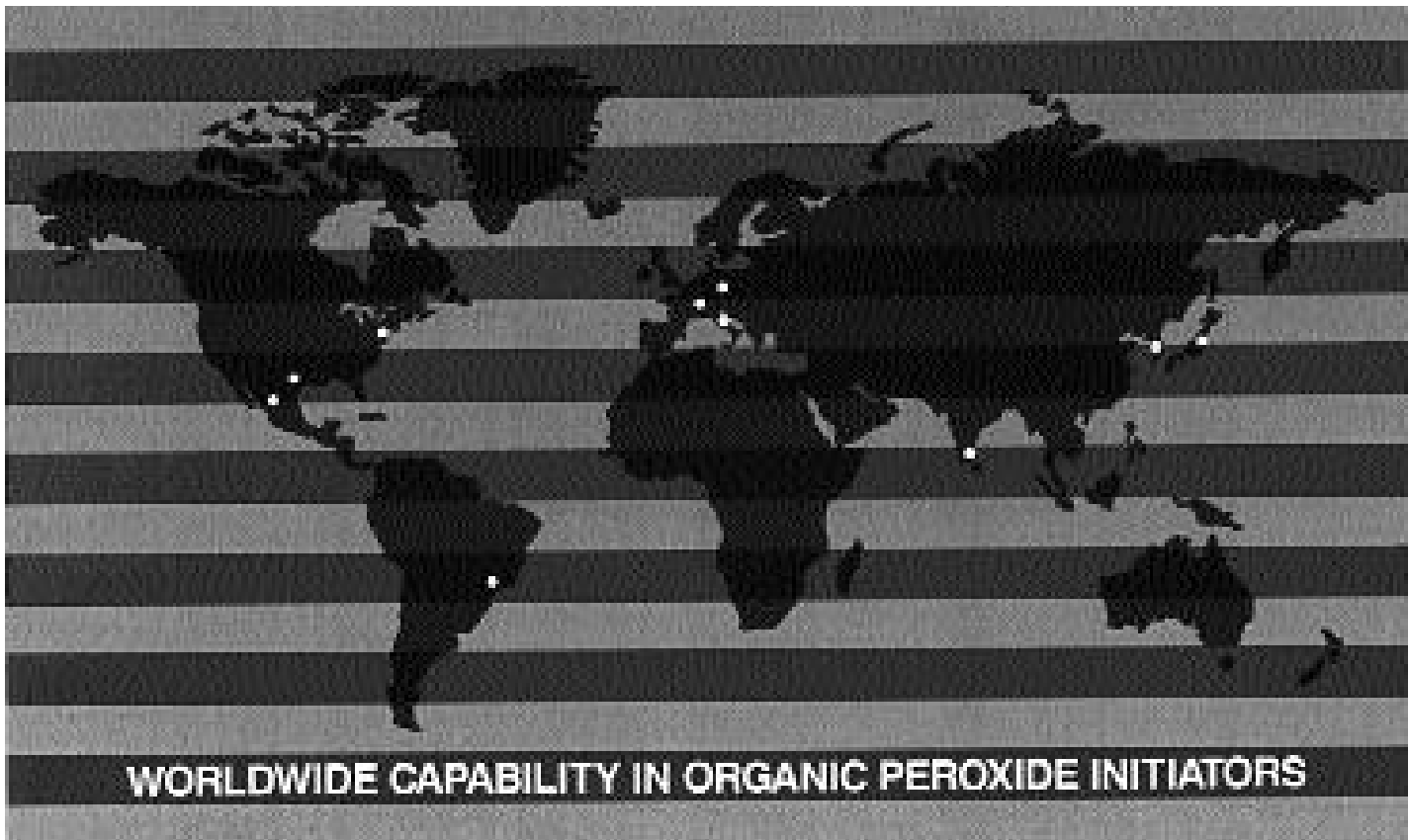
MATERIAL SAFETY DATA SHEETS

SAFETY BULLETIN "ORGANIC PEROXIDES:
THEIR SAFE HANDLING AND USE"

LITERATURE PACKAGE: "POLYESTER"

HALFLIFE® BULLETIN: "PEROXIDE SELECTION
BASED ON HALF-LIFE"

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Remember the Rules for Safety
Safe use of organic peroxide initiators

- Leave room for cool air circulation in storage.
- Rotate inventory: "first in, first out."
- Know your plant's emergency procedures.
- Take only what you will be using.
- Clean up spills. Dispose of them properly.
- Control the temperature of all equipment.
- Protect your eyes and skin.
- Read the label and material safety data sheet (MSDS) for every peroxide you use.
- Keep peroxide away from flames and sparks.
- Avoid contamination.

These are the keys to safe handling of peroxides. When care is taken, cross-linking elastomers and polyolefins with peroxides will be a problem-free and safe procedure.

EMERGENCY RESPONSE NUMBER

CHEMTREC 800-424-9300
 from Canada 202-483-7616

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