



ORGANIC PEROXIDES



**Crosslinking rubber,
elastomer and polyethylene**



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Research center of Lyon

A global chemical player, Arkema consists of 3 coherent and balanced business segments:

- **Vinyl Products:** Chlorochemicals and PVC, Vinyl Compounds, Pipes and Profiles.
- **Industrial Chemicals:** Acrylics, PMMA, Thiochemicals, Fluorochemicals, Hydrogen Peroxide.
- **Performance Products:** Technical Polymers, Specialty Chemicals, Organic Peroxides, Additives, Urea Formaldehyde Resins, Agrochemicals.

Arkema develops its activities by combining safety and environmental protection, client proximity, industrial reliability, and competitiveness.

Present in over 40 countries with 18,600 employees, Arkema achieves sales of 5.2 billion euros.

With its six research centers in France, the United States and Japan, and internationally recognized brands, Arkema holds leadership positions in its principal markets.

Research center of Philadelphia

Luperox[®] Organic Peroxides and polymers

Peroxides crosslinking

Organic Peroxides can be thermally decomposed to generate free radicals which can subsequently create an active site on a polymer backbone. The reaction between two active sites will create a strong link between the polymer chains, leading to a polymer network exhibiting very desirable mechanical properties, in particular excellent heat resistance and compression set. Among the other advantages offered by Organic Peroxides versus sulfur vulcanization is the wide range of polymers which can be crosslinked (unsaturated polymers as well as saturated polymers like polyethylene). Due to the nature of the strong carbon-carbon crosslink bond created by the use of Organic Peroxides, it is possible to utilize the full engineering capabilities of these peroxide crosslinkable polymers.

Polymers which can be crosslinked with Organic Peroxides

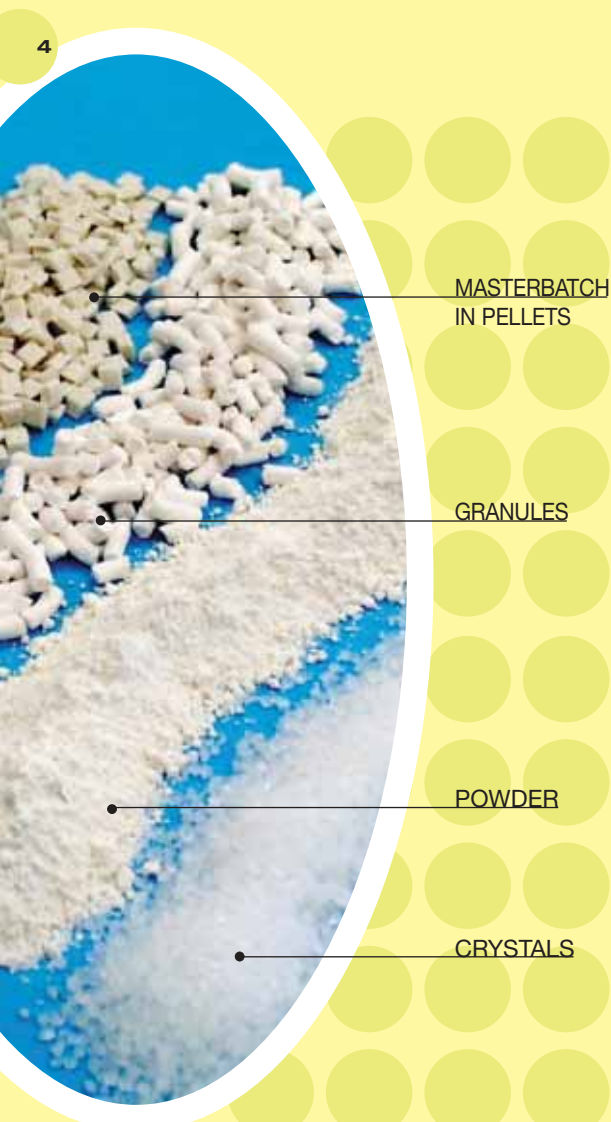
| | |
|--------------|---|
| ABS | Acrylonitrile butadiene styrene copolymer |
| AU/EU | Polyurethane rubber |
| BR | Polybutadiene rubber |
| CM | Chlorinated polyethylene |
| CR | Polychloroprene rubber |
| CSM | Chlorosulfonyl polyethylene |
| EBA | Ethylene butylacrylate copolymer |
| EPM | Ethylene propylene copolymer |
| EPDM | Ethylene propylene diene terpolymer |
| EVA | Ethylene vinylacetate copolymer |
| FPM | Fluoro rubber |
| HNBR | Hydrogenated butadiene acrylonitrile rubber |
| IR | Polyisoprene rubber |
| NBR | Butadiene acrylonitrile rubber |
| NR | Natural rubber |
| PE | Polyethylene |
| POE | Polyolefin elastomer |
| Q | Silicone rubber |
| SBR | Styrene butadiene rubber |
| T | Polysulfide rubber |
| EEA | Ethylene ethyl acrylate |

Polymers which can not be crosslinked with Organic Peroxides

| | |
|-------------|---------------------------|
| ACM | Polyacrylate rubber |
| CIIR | Chlorobutyl rubber |
| CO | Epichlorohydrin rubber |
| ECO | Epichlorohydrin copolymer |
| IIR | Butyl rubber |
| PB | Polybutene-1 |
| PIB | Polyisobutene |
| PVC | Polyvinylchloride |
| PP | Polypropylene |

Suggested technology to mix with Luperox[®] Organic Peroxides

| | liquid or liquefiable grades | granules | powder grades | masterbatch grades |
|---|------------------------------|----------|---------------|--------------------|
| absorption on polymer | + | - | - | - |
| internal mixer | - | + | + | + |
| open mill | - | + | - | + |
| direct extruder injection | + | - | - | - |
| direct screw compounding without injection | - | - | - | + |



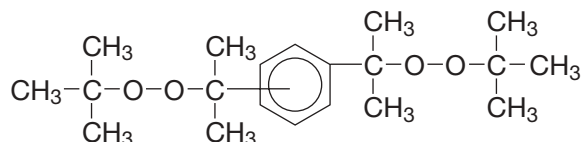
Luperox® Organic Peroxide

Physico-chemical properties and chemical structures for the key crosslinking peroxides

LUPEROX® F

1,3 1,4-Bis(*tert*-butylperoxyisopropyl)benzene
Cas N° 25155-25-3

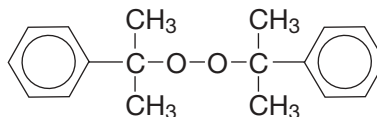
Molecular weight: 338.5 g
Melting point: 41°C
Active oxygen: 9.45%



LUPEROX® DC

Dicumyl peroxide
Cas N° 80-43-3

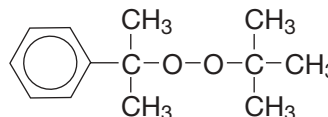
Molecular weight: 270.4 g
Melting point: 39°C
Active oxygen: 5.92%



LUPEROX® 801

tert-butylcumylperoxide
Cas N° 3457-61-2

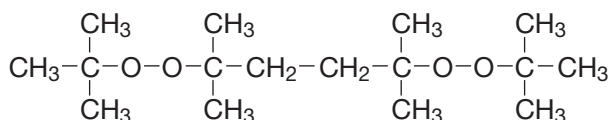
Molecular weight: 208.3 g
Melting point*: 6°C
Active oxygen: 7.68%



LUPEROX® 101

2,5-dimethyl-2,5-di-(*tert*-butylperoxy)hexane
Cas N° 78-63-7

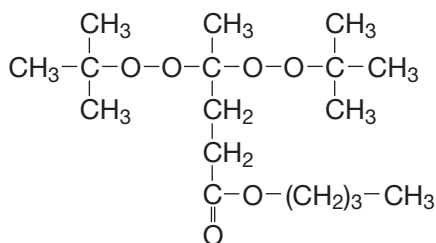
Molecular weight: 290.4 g
Melting point*: 5°C
Active oxygen: 11.02%



LUPEROX® 230

n-butyl-4,4'-di-(*tert*-butylperoxy)valerate
Cas N° 995-33-5

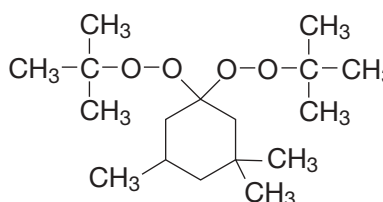
Molecular weight: 334.4 g
Active oxygen: 9.57%
Note: this product exists only as extended grade



LUPEROX® 231

1,1'-di(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane
Cas N° 6731-36-8

Molecular weight: 302.4 g
Active oxygen: 10.58%
Note: this product exists only as extended grade



Note*: these products exhibit supercooling phenomena in a wide range of temperature below melting point, i.e. the product can be stored for a period of time below the melting point and remain liquid.

Kinetic data

Half-Life Time

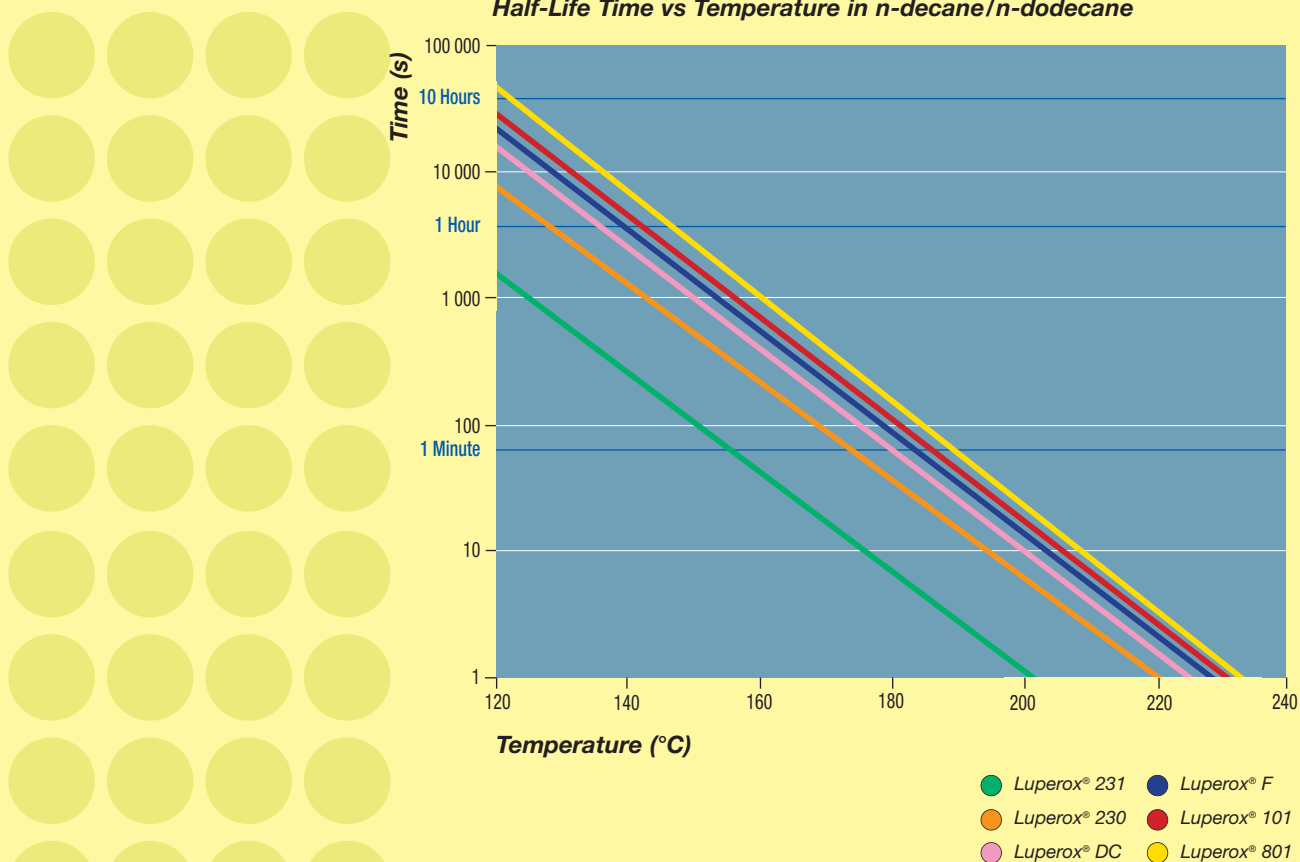
The **half-life** of a peroxide at any specified temperature is the time required at that temperature to affect a loss of one half of the peroxide's active oxygen content. The rate of crosslinking produced by a free radical initiator will be determined by its **rate of thermal decomposition**. Half-life data is essential for selecting the optimum initiator for specific time-temperature applications. Peroxide half-life data are generated by studying their thermal decomposition in various solvents at low concentrations. The polarity of the solvent used in these studies will influence the peroxide decomposition kinetics. Thus it is important to compare peroxide half-life data generated in the same solvent and at the same concentration and, preferably when the initiators are of the same class. Producers of initiators and their customers roughly correlate the **thermal stability** of initiators with temperature. It is useful to express this stability in terms of 1 min, 1 hr and 10 hrs half-life temperatures, i.e., the temperatures at which 50% of the initiator has decomposed in 1 min, 1 hr and 10 hrs, respectively.

Examples: In a fixed time of 1 minute, 50% of Luperox® 231 is decomposed at 155°C.

The same time is required to decompose 50% of Luperox® DC at 180°C.

At a fixed temperature of 170°C, about 2 min 40 s are necessary to decompose half of Luperox® F.

Half-Life Time vs Temperature in n-decane/n-dodecane



Selection

Luperox® Organic Peroxide dosage level recommendations in phr* for various crosslinkable polymers and elastomers.

Dosage of LUPEROX® Organic Peroxides in some polymers. phr of active substance

| | LUPEROX® F | LUPEROX® DC | LUPEROX® 101 | LUPEROX® 801 | LUPEROX® 230 | LUPEROX® 231 |
|--|----------------------|-----------------------|------------------------|------------------------|------------------------|------------------------|
| LDPE Low density polyethylene | 1.2-1.8 | 1.5-2.5 | 1.4-2.0 | 1.2-2.0 | - | - |
| HDPE High density polyethylene | - | - | 0.5-1.2 | - | - | - |
| EVA Ethyl-vinyl acetate | 0.8-1.6 | 1.2-2.0 | 1.0-1.8 | 1.0-1.6 | 1.4-2.6 | 1.2-2.3 |
| EPM/EPDM Ethylene-propylene monomers | 1.6-3.2 | 2.4-5.4 | 1.7-3.4 | - | 3.2-6.3 | 2.4-6.0 |
| CM Chlorinated polyethylene | 1.5-2.4 | 2.4-3.8 | 2.5-4.0 | - | 3.3-6.0 | 3.0-5.5 |
| Q Silicone rubber | 0.2-1.0 | 0.5-2.0 | 0.4-1.5 | - | - | - |
| NBR Butadiene acrylonitrile rubber | 0.5-1.5 | 0.9-1.7 | 1.1-2.0 | - | 1.2-2.2 | 1.0-2.0 |
| SBR Styrene butadiene rubber | 0.4-1.0 | 0.7-1.5 | 0.7-1.2 | - | 0.8-1.8 | 0.7-1.6 |

Example: Typically, 1.6 to 3.2 phr of Luperox® F are used in an EPM/EPDM compound.

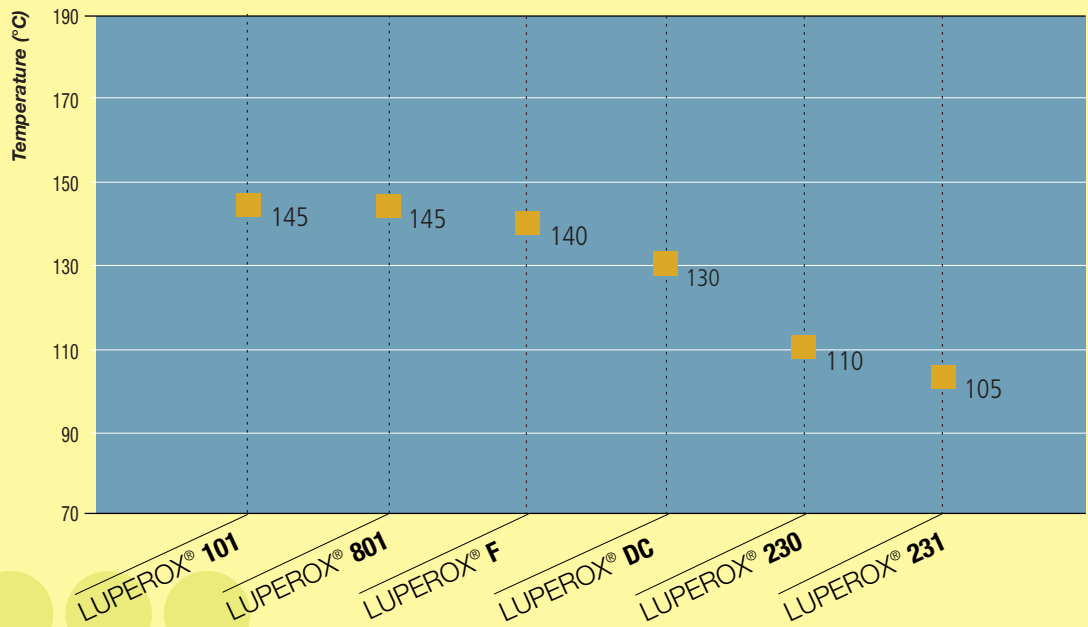
For a formulated peroxide, this quantity has to be divided by the peroxide content.

Therefore, 4 to 8 phr of Luperox® F40 is the typical range of quantities utilized for an EPM/EPDM compound.

Note:* part per hundred rubber - The phr values are based on a pure basis for each peroxide. When using a lower assay, extended grades, one must adjust the quantity of the grade considered. Please see the example provided above.

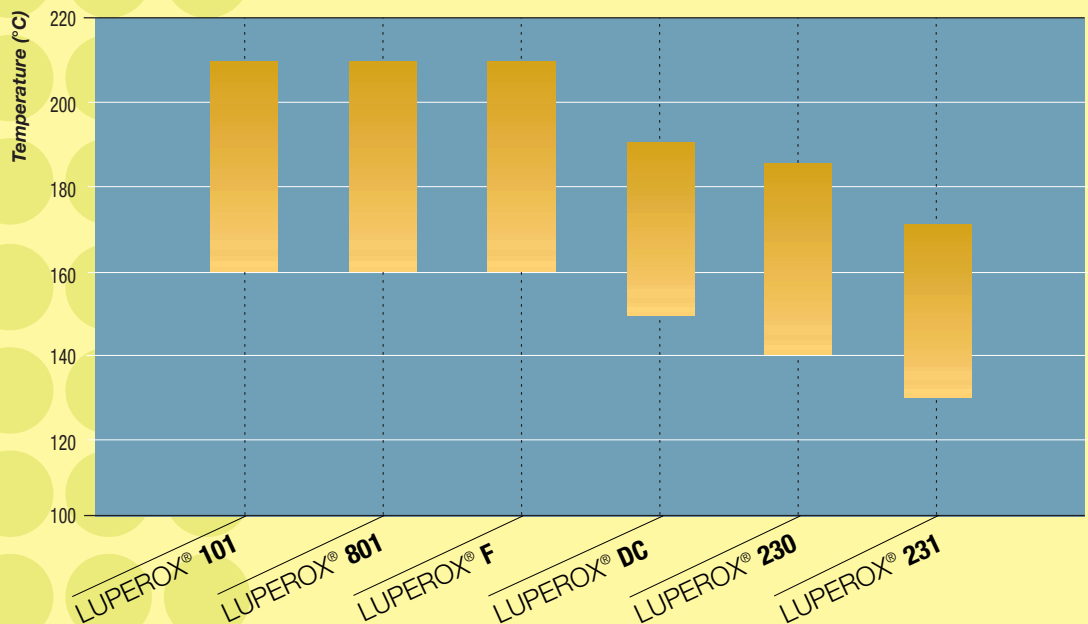
Suggested maximum compounding temperature

Example: The suggested maximum compounding temperature is the temperature at which the scorch time (t_{S05})* is equal to 5 minutes. If this temperature is exceeded during compounding the peroxide could decompose and lead to undesired crosslinking.



Suggested curing temperature range

Example: It is recommended to cure a polymer with Luperox® F at a temperature between 160°C and 210°C.



Note*: see page 10 for definition.

Selection

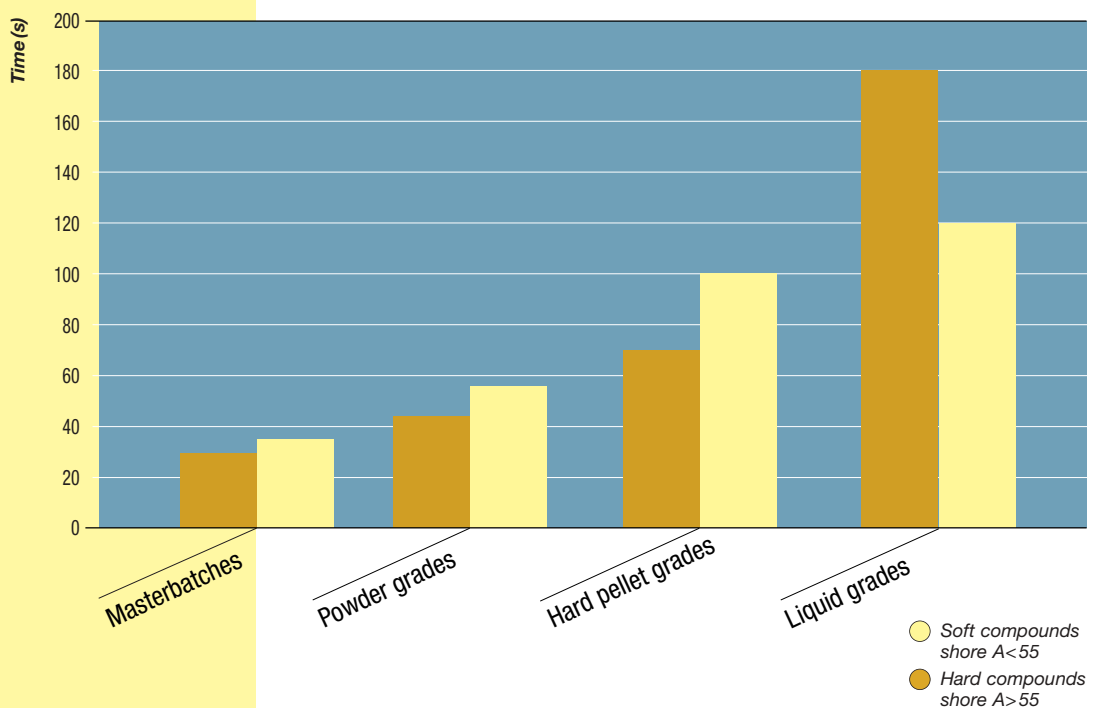
Suggested compounding time in rubber industry

Experiments were performed with an EPDM compound in a Brabender type internal mixer.

Standard deviation of M_H was determined using an ODR2000E rheometer after different times of compounding. The times reported in this graph are the mixing times required to obtain an acceptable standard deviation in M_H from batch to batch, comparing the various commercially available forms of di-(t-butylperoxy)diisopropylbenzene.

Pre-dispersed peroxide **masterbatches** dramatically **shorten mixing time** and improve the quality of the elastomer by avoiding premature crosslinking or “scorch” in hard or soft compounds. The final elastomeric composition exhibits a desirably lower and more consistent viscosity, essential to molding and extrusion operations. **Consistency in the final physical properties** of crosslinked technical articles is obtained via these peroxide masterbatches, as they create factory compounds with an exceptionally **uniform peroxide dispersion**.

Example: Peroxides in masterbatch form like Luperox® F40ED significantly reduce the compounding time in hard and soft compounds.



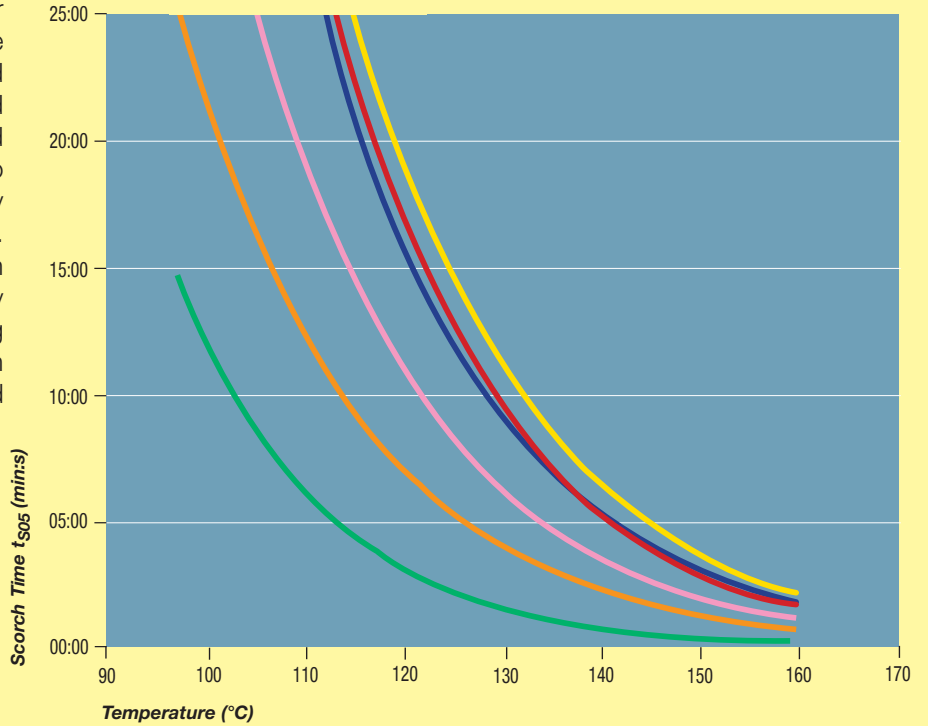
Performances

Processing time information

Experimental data were generated using a Mooney viscometer. t_{S05} is the scorch time at the processing temperature (usually at the polymer extrusion temperature). This value represents the time during which the vulcanizable compound can be safely processed before unwanted crosslinking or “scorch” takes place. t_{S05} is defined as the time needed at a specific temperature to obtain a 5 Mooney Unit increase in the viscosity as measured from the MV or minimum viscosity. It gives to the user valuable information on process safety. It is important to note that any premature crosslinking generated during compounding is not reversible, it can lead to an undesirable increase in elastomer viscosity and finally to a non meltable polymer.

Example: If an EPDM compound containing Luperox® F is processed at 130°C, its viscosity will be increased by 5 Mooney Units after about 10 minutes.

Mooney Scorch t_{S05} vs Temperature in an EPDM compound



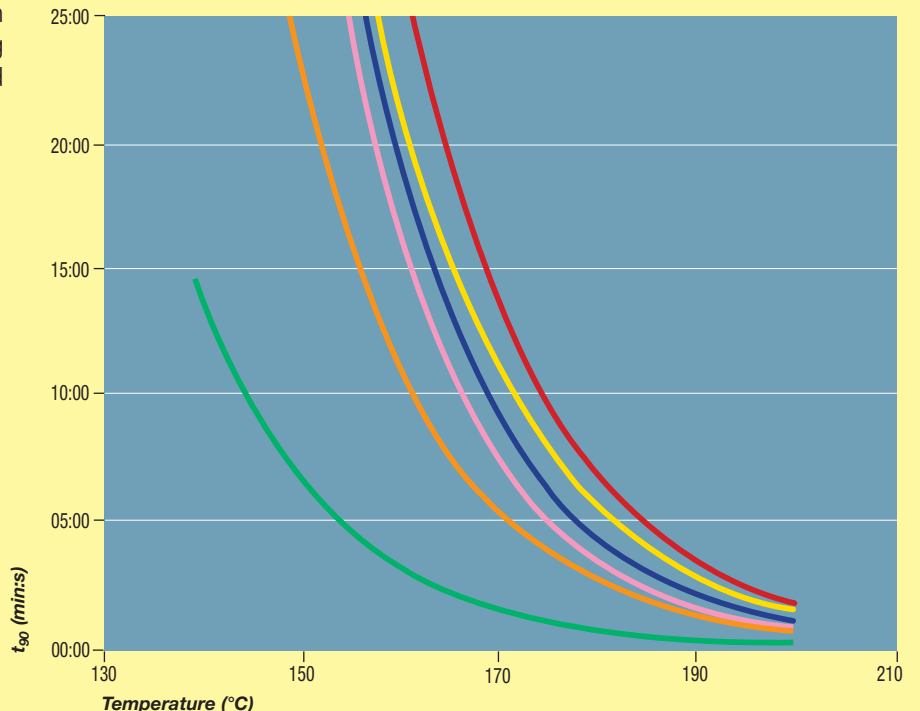
- Luperox® 231
- Luperox® 230
- Luperox® DC
- Luperox® F
- Luperox® 101
- Luperox® 801

Cure time information

Experimental data were recorded using an ODR2000E rheometer. t_{90} represents the time needed to reach 90% of the difference between the maximum and the minimum crosslinking density. t_{90} is one of the key parameters used to study improvements in productivity.

Example: 90% of the crosslinking density of an EPDM compound cured with Luperox® F at 170°C will be obtained after 9 minutes. It will take 3 minutes at 185°C to obtain the same result.

t_{90} vs Temperature in an EPDM compound



Influence of compounding additives



Coagents

Coagents, or crosslinking activators, are used to increase the crosslinking efficiency of the peroxide. Among the coagents, one can mention sulfur, provided its dosage does not exceed 0.3 phr. Other commonly used coagents comprise:

- triallylcyanurate/triisocyanurate
- trimethylpropanetrimethacrylate
- ethyleneglycoldimethacrylate
- m-phenylene dimaleimide
- 1, 2-cis-polybutadiene

TAC/TAIC
TRIM or TMPTM
EDMA

The use of these coagents (recommended dosage: 1 to 3% related to rubber) typically leads to an increase of hardness and tensile strength, a decrease of the elongation at break and an improvement of the compression set (except with sulfur).

Antioxidants

Antioxidants, also known as antidegradants, are designed to protect vulcanizates from various external degrading influences which could significantly affect the service life. Oxidative degradation can be prevented by the use of appropriate antioxidants. Their role is to scavenge oxy radicals prior to undesired reactions with the rubber. These antioxidants are usually secondary aromatic amines or hindered phenols.

Among the antioxidants (recommended dosage: 1 to 2% related to rubber) used with Organic Peroxides, one can mention:

- 2-mercapto benzimidazole
- polymerized 1,2-dihydro-2,2,4-trimethylquinoline
- hydroquinone monomethyl ether
- mono *tert*-butyl hydroquinone
- 2,5-di(*tert*-amyl) hydroquinone

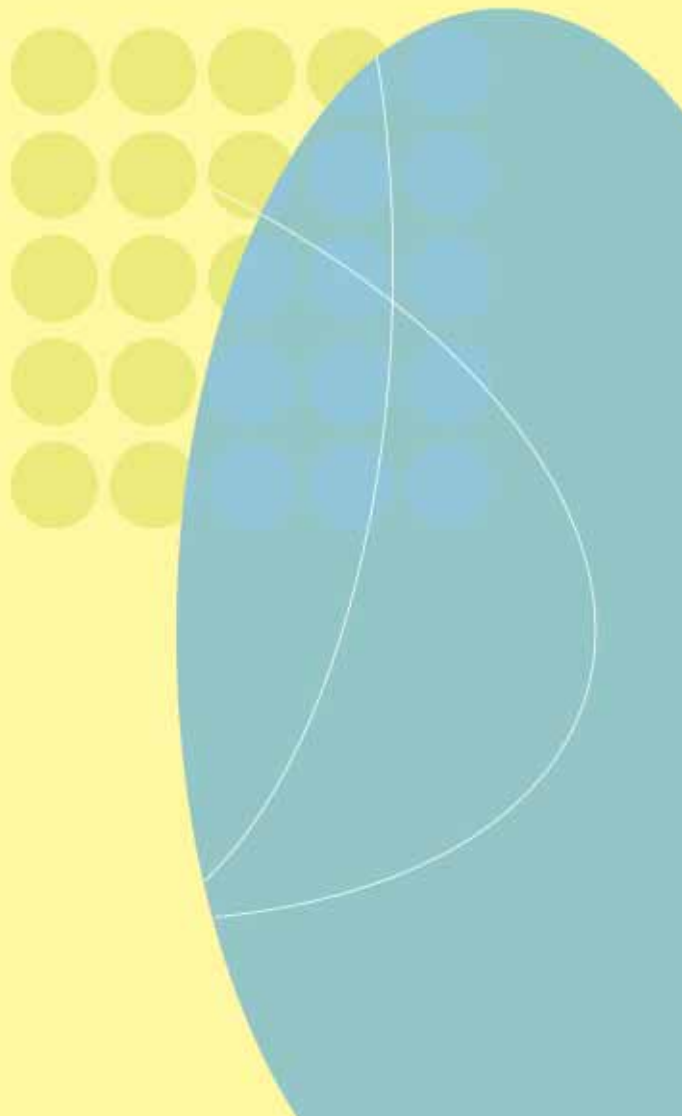
MBI
TMQ
HQMME
MTBHQ
DTAHQ

Plasticizers

These additives can be used as processing aids, extenders (lower the compound cost) and as active ingredients capable of imparting special properties to vulcanizates. It has to be mentioned that some of these additives, especially aromatic oils, are not recommended as they may consume some of the radicals generated by the Organic Peroxides. In this regard, paraffinic type oils are preferred.

Fillers

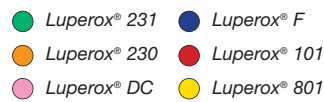
Reinforcing and non reinforcing fillers can be used in compounds cured with peroxides. These fillers can be carbon black, silicates, silica, kaolin clay, calcium carbonate. However, acidic fillers known as “channel” carbon blacks, “hard clay” and acidic silicas may initiate ionic decomposition of the peroxide. If the use of these fillers is necessary, it is advisable to neutralize the compound with small quantities of basic metallic oxides (MgO, ZnO) or with amines (DPG, hexamethylene tetramine, triethanolamine).



Performances

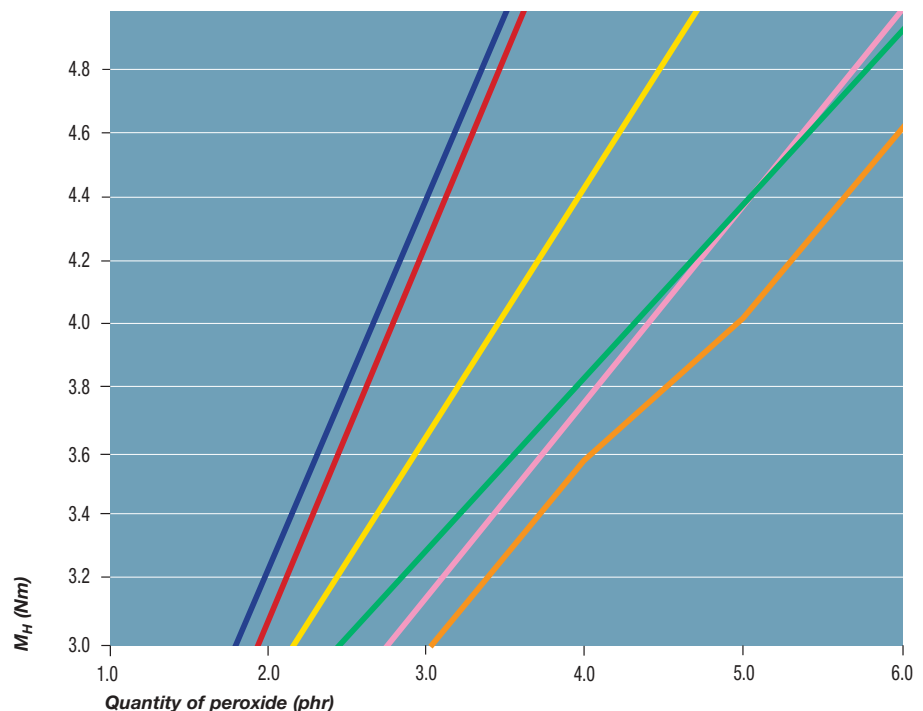
Crosslinking efficiency information

These data were generated using an ODR2000E rheometer. M_H (Nm) is a torque measurement which is proportional to the relative amount of crosslinking bonds created by the peroxide. It is an indication of the mechanical properties to be expected.



Example: When curing EPDM at 185°C, our data suggest that only 2.6 phr of pure Luperox® F are required to provide the same level of crosslink density as 4.3 phr of pure Luperox® DC.

**Crosslinking of an EPDM compound at 185°C
(except for Luperox® 231: 170°C)**



Luperox® Organic Peroxide main crosslinking products range

| PEROXIDES Commercial name | PURE PEROXIDES | | INERT FLEGMATISED PEROXIDES | | MASTERBATCH POLYMER PREDISPERSION (300 microns filtered) | |
|------------------------------|----------------|-------------------|-----------------------------|-------------------|--|--------------------|
| | liquid | flakes | granules | powder | pellets | sheets |
| LUPEROX® F | | LUPEROX® F FLAKES | | | | |
| | | | | LUPEROX® F90P | | |
| | | | LUPEROX® F40 | LUPEROX® F40P | | |
| | | | LUPEROX® F40KE | LUPEROX® F40KEP | | |
| | | | | | LUPEROX® F40MG | LUPEROX® F40MF |
| | | | | | LUPEROX® F40MG EVT | LUPEROX® F40MF EVT |
| | | | | | LUPEROX® F40ED | LUPEROX® F40EDF |
| LUPEROX® DC | | LUPEROX® DCP | | | | |
| | | | | LUPEROX® DC92P | | |
| | | | LUPEROX® DC40 | LUPEROX® DC40P | | |
| | | | LUPEROX® DC40KE | LUPEROX® DC40KEP | | |
| | | | | | LUPEROX® DC40MG | LUPEROX® DC40MF |
| | | | | | LUPEROX® DC40MGF | LUPEROX® DC40MFF |
| | | | | | LUPEROX® DC40MGPE | |
| LUPEROX® 101 | LUPEROX® 101 | | | | | |
| | | | | LUPEROX® 101XLS50 | | |
| | | | | LUPEROX® 101XL45 | | |
| | | | | | LUPEROX® 101MG40 | LUPEROX® 101MF40 |
| LUPEROX® 801 | LUPEROX® 801 | | | | | |
| LUPEROX® 230 | | | LUPEROX® 230XL40 | | | |
| LUPEROX® 231 | | | LUPEROX® 231G40 | LUPEROX® 231XL40 | | |
| | | | | | LUPEROX® 231MG40 | LUPEROX® 231MF40 |

| PEROXIDE CONTENT | CARRIER | STANDARD PACKAGING |
|------------------|--|---|
| % | | |
| 90 | SiO ₂ | 20 kg in carton box |
| 40 | CaCO ₃ | 20 kg in carton box |
| 40 | kaolin | 20 kg in carton box |
| 40 | EPM | 25 kg in carton box or 20 kg in big box |
| 40 | EPDM + EVA + SiO ₂ | 25 kg in carton box or 20 kg in big box |
| 40 | EPM + CaCO ₃ + SiO ₂ | 25 kg in carton box or 20 kg in big box |
| 98 | | 20 kg in carton box |
| 92 | SiO ₂ | 20 kg in carton box |
| 40 | CaCO ₃ | 20 kg in carton box |
| 40 | kaolin | 20 kg in carton box |
| 40 | EPM | 25 kg in carton box or 20 kg in big box |
| 40 | EPM + CaCO ₃ + SiO ₂ | 25 kg in carton box or 20 kg in big box |
| 40 | EPM + LDPE | 25 kg in carton box or 20 kg in big box |
| >94 | | 25 kg in plastic bin |
| 50 | SiO ₂ | 25 kg in carton box |
| 45 | CaCO ₃ + SiO ₂ | 25 kg in carton box |
| 40 | EPM + SiO ₂ | 25 kg in carton box |
| 94 | | 25 kg in plastic bin |
| 40 | CaCO ₃ + SiO ₂ | 25 kg in carton box |
| 40 | CaCO ₃ + SiO ₂ | 25 kg in carton box |
| 40 | EPM + SiO ₂ | 25 kg in carton box |



Specific hazards and safe handling

Organic Peroxides are characterised by an oxygen-oxygen bond in their molecular structure.

Certain conditions involve the cleavage of this bond, creating very reactive free radicals.

Due to this high reactivity, Organic Peroxides require special care and attention when being handled and stored.

Therefore, Organic Peroxides must be handled only by personnel well informed on safety conditions who should always refer to the safety data sheet before handling the product.

Physical and chemical hazards

Main causes of peroxide decomposition are heat, fire and chemical contamination.

According to European and US regulations, our peroxides have been tested to assess the hazards related to flammability, sensitivity to shock and heat.

Flammability

Organic Peroxides are highly flammable, contact with combustible material may cause fire.

Thermal decomposition creates flammable and harmful products.

- All sources of sparks and ignition must be prohibited; smoking must be forbidden.
- Fire must be extinguished with water spray and foam. Specific methods to put out the fire are given in the safety data sheet.

Among the dialkyl peroxides, LUPEROX® DI (Di-*tert*-butylperoxide), due to its very low flash point, must be handled as a flammable liquid.

Heat sensitivity

Organic Peroxides are sensitive to heat and above a certain temperature, their decomposition becomes uncontrolled. The self accelerating decomposition temperature (SADT) provides a measure of this hazard and is used to determine the maximum allowable storage and transport temperature.

- Storage temperature must be controlled.

Contamination

Chemical contamination can accelerate decomposition of Organic Peroxides.

- Avoid contact with oxidizing and reducing agents, metal salt, acids and bases.
- Never return unused product to the original container.

Health risks and personnel protection

Some of the dialkyl peroxides are skin and eye irritants and the necessary handling precautions should be observed i.e:

- specific protection must be used when handling these products: wear gloves, safety glasses or goggles, protective clothing;
- avoid contact with skin and eyes; avoid inhalation of vapours.

Safe storage

Proper storage is critical to the safe handling of Organic Peroxides.

Storage is subjected to national and local regulations concerning such activities in terms of safety and protection of the environment.

These regulations must be carefully checked before storing Organic Peroxides.

Storage facilities

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

- located in an isolated area;
- used only for the storage of Organic Peroxides;
- explosion-proof;
- free of all combustible material.

Storage temperature

The best way to avoid decomposition due to heat is to strictly respect the recommended storage temperature.

Keep at temperatures below 30°C. Peroxides must be stored in their original packages.

Storage and transport

Transport and packaging

Transport

Transport of Organic Peroxides is governed by national and international regulations. Organic peroxides are classified according to the degree of hazard they present; they belong to the specific class 5.2.

The control temperature and emergency temperature are derived from the SADT*. Due to their high SADT, dialkyl peroxides do not require refrigerated transport. However, to maintain the quality of the peroxides, the maximum transport temperature has to be kept below 30°C.

Packaging

Packaging methods and maximum capacity allowed in packaging are also described in the transport regulations, depending on the peroxide characteristics. Regulation information related to handling and transport is given on the package labels. A model of label is given below.



Note*: Self Accelerating Decomposition Temperature.



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