Selecting the right initiator

A survey of commonly used organic peroxides for reinforced plastics fabrication

Introduction

Initiators for Thermoset Polymers

Akzo Nobel is the world’s largest producer of initiators for free radical polymerization of various monomers.

This product catalog lists many Akzo Nobel initiators for curing thermoset resins, coatings, speciality monomers and resins. These initiators are marketed under such well-known trademarks as Trigonox®, Perkadox®, Laurox® and Cadox®. The largest part of our initiators consists of organic peroxides (O-O initiators) which can be categorized into peroxy (di) carbonate, peroxyesters, diacylperoxides, peroxyketals, dialkyl peroxides and hydroperoxides. In addition, we supply Azo (N-N) and C-C initiators.

Main areas of application include curing of unsaturated polyester and vinyl ester resins used in manufacture of fiberglass reinforced plastics (FRP) such as bathroom fixtures, automotive body parts, chemical storage tanks, pipes and liners, furniture, boat hulls, fishing rods, light weight ladder rails, RV parts and architectural components.
Our leadership in the FRP industry is maintained through modern manufacturing techniques, high quality standards, leadership in organic peroxide safety, active technical support, and efficient marketing, sales and distribution systems. Our organic peroxides are produced domestically in Burt (NY), Pasadena (TX) and Los Reyes (Mexico). From these plants and other strategically located warehouses and distributors, we serve all major markets in North America. In many cases, products can be shipped via our own fleet of specially designed, temperature controlled trucks.

This is all overseen by our centrally located North American headquarters in Chicago (IL) which serves customer service, sales and marketing needs. Technical support can be obtained from our Chicago headquarters and our supporting Research Centers, manufacturing facilities & sales offices around the world.

Our philosophy of partnering with our customers to optimize performance and minimize end use cost combined with our thermoset experience provides one of the biggest resources available to the FRP industry. We would like to extend an opportunity to optimize applications, improve efficiencies, resolve difficulties or even design new initiator systems by meeting to discuss your requirements.
## Ambient Temperature Catalysts

### Ketone peroxides

<table>
<thead>
<tr>
<th>Product name</th>
<th>Chemical description</th>
<th>Active Oxygen (%)</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadox D-50</td>
<td>Methyl ethyl ketone peroxide solution in 2,2,4-</td>
<td>9</td>
<td>• Standard, general purpose MEKP</td>
</tr>
<tr>
<td>Cadox D-30</td>
<td>trimethyl-1,3-pentanediol diisobutanoate</td>
<td>5.3</td>
<td>• Useful in all ambient temperature processes (hand lay-up, spray-up, casting, RTM)</td>
</tr>
<tr>
<td>Cadox L-50a</td>
<td>Methyl ethyl ketone peroxide, solution in 2,2,4-</td>
<td>9</td>
<td>• Specially formulated MEKP for gel coat and vinyl ester resin applications</td>
</tr>
<tr>
<td>Cadox L-30a</td>
<td>trimethyl-1,3-pentanediol diisobutanoate</td>
<td>5.3</td>
<td>• Excellent through-cure</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Long gel times and pot life</td>
</tr>
<tr>
<td>Cadox M-50a</td>
<td>Methyl ethyl ketone peroxide solution in plasticizer</td>
<td>9</td>
<td>• Higher reactivity than Cadox L-50a in GP/ISO resins</td>
</tr>
<tr>
<td>Cadox M-30a</td>
<td></td>
<td>5.3</td>
<td>• Shorter gel time than Cadox D-50 or Cadox L-50a</td>
</tr>
<tr>
<td>Trigonox 44B</td>
<td>Acetylacetone peroxide, in solvent mixture</td>
<td>4</td>
<td>• Longer gel times, faster gel-to-peak than MEKP</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Improved pot life without sacrificing cure</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Provides faster cure, quicker mold turnover</td>
</tr>
<tr>
<td>Trigonox 61a</td>
<td>Mixture of methyl ethyl ketone peroxide and acetylacetone</td>
<td>7.7</td>
<td>• Similar gel time to Cadox M-50a with master cure speed</td>
</tr>
<tr>
<td></td>
<td>peroxide, in solvent mixture</td>
<td></td>
<td>• Increased productivity over standard MEKP in casting applications</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Higher efficiency in standard open molding processes</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Can be used in gel coats (this should be tested first)</td>
</tr>
<tr>
<td>Trigonox 63a</td>
<td>Methyl ethyl ketone peroxide and acetylacetone peroxide,</td>
<td>6.5</td>
<td>• Slightly slower gel time than Trigonox 61a with faster cure speed</td>
</tr>
<tr>
<td></td>
<td>in solvent mixture</td>
<td></td>
<td>• Excellent in polymer concrete applications</td>
</tr>
<tr>
<td>Trigonox 178</td>
<td>Methyl ethyl ketone peroxide and cumyl hydroperoxide</td>
<td>8.8</td>
<td>• Lower exotherm than Standard MEKP’s</td>
</tr>
<tr>
<td></td>
<td>solution in 2,2,4-trimethyl-1,3-pentanediol diisobutanoate</td>
<td></td>
<td>• Useful in warm and hot weather climates</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Suitable for open molding and spray-up applications</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Ideal for thick laminates processing</td>
</tr>
<tr>
<td>Trigonox 263</td>
<td>Methyl ethyl ketone peroxide and cumyl hydroperoxide,</td>
<td>8.8</td>
<td>• Lower exotherm than Standard MEKP’s</td>
</tr>
<tr>
<td></td>
<td>solution in 2,2,4-trimethyl-1,3-pentanediol diisobutanoate</td>
<td></td>
<td>• Slightly faster than Trigonox 178</td>
</tr>
<tr>
<td>Product name</td>
<td>Chemical description</td>
<td>Active Oxygen (%)</td>
<td>Peroxide content (%)</td>
</tr>
<tr>
<td>--------------</td>
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<td>-------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>Perkadox 40E</td>
<td>Dibenzoyl peroxide, 40% suspension with diisobutyl phthalate</td>
<td>2.6</td>
<td>40</td>
</tr>
<tr>
<td>Perkadox 40ES</td>
<td>Dibenzoyl peroxide, 40% suspension with diisobutyl phthalate</td>
<td>2.6</td>
<td>40</td>
</tr>
<tr>
<td>Perkadox BTW-50</td>
<td>Dibenzoyl peroxide, paste, 50% in dipropylene glycol dibenzoate and water</td>
<td>3.3</td>
<td>50</td>
</tr>
<tr>
<td>Perkadox BTW-55</td>
<td>Dibenzoyl peroxide, paste, 55% in solvent mixture</td>
<td>3.6</td>
<td>55</td>
</tr>
<tr>
<td>Perkadox CH-50</td>
<td>Dibenzoyl peroxide, powder, 50% with dicyclohexyl phthalate</td>
<td>3.3</td>
<td>50</td>
</tr>
<tr>
<td>Perkadox L-W75</td>
<td>Dibenzoyl peroxide, powder, 75% with water</td>
<td>4.6</td>
<td>75</td>
</tr>
</tbody>
</table>
### Cumyl hydroperoxides

<table>
<thead>
<tr>
<th>Product name</th>
<th>Chemical description</th>
<th>Active Oxygen (%)</th>
<th>Applications</th>
</tr>
</thead>
</table>
| **Trigonox 239** | Cumyl hydroperoxide, 45% solution in solvents | 4.6 | • Specific for vinyl ester resins  
• Eliminates foaming common to MEKP’s  
• Efficient in both single/dual promoted systems |
| **Trigonox K-90** | Cumyl hydroperoxide, 90% in aromatic solvent mixture | 9.3 | • Reduces exotherm in thick walled parts  
• Also useful in pultrusion applications |
| **Trigonox A-W70** | tert-Butyl hydroperoxide, 70% solution in water | 12.4 | • Reduces exotherm in thick walled parts  
• More efficient than *Trigonox* K-90 |

### New products

<table>
<thead>
<tr>
<th>Product name</th>
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<th>Peroxide content (%)</th>
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</tr>
</thead>
</table>
| **Trigonox 93** | tert-Butyl peroxybenzoate, 80% solution with acetylacetone | 6.5 | 80 | • Can be used with cobalt salt to cure unsaturated polyester resins at 60°C and above  
• Useful for pultrusion, RTM and panel |
| **Trigonox 524** | Mixture of acetylacetone peroxide and tert-butyl peroxybenzoate in solvents | 4.7 | 47 | • For ambient and elevated cure systems exceeding 60°C peak exotherms  
• Faster gel & cure than *Trigonox* 93  
• Can be combined with promoters to accelerate cure  
• Most effective at reducing residual styrene and benzaldehyde  
• Ideal for RTM, panel, filament winding and continuous laminating |
## Peroxyesters

<table>
<thead>
<tr>
<th>Product name</th>
<th>Chemical description</th>
<th>Active Oxygen (%)</th>
<th>Peroxide content (%)</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Trigonox 21S</em></td>
<td>tert-Butyl peroxy-2-ethylhexanoate</td>
<td>7.2</td>
<td>97</td>
<td>• Pure form, direct sales only</td>
</tr>
</tbody>
</table>
| *Trigonox 21-C50* | tert-Butyl peroxy-2-ethylhexanoate, 50% in odorless mineral spirits | 3.7               | 50                   | • Plasticizer free formulation  
• Temperature-controlled transport and storage                                                                                             |
| *Trigonox 21-OP50* | tert-Butyl peroxy-2-ethylhexanoate, 50% in dioctyl phthalate | 3.7               | 50                   | • Liquid alternative to BPO for non-promoted systems  
• Standard intermediate initiator  
• Slightly higher storage temperature than *Trigonox 21-C50*                                                                                   |
| *Trigonox 42S* | tert-Butyl peroxy-3,5,5-trimethylhexanoate                    | 5.9               | 97                   | • Intermediate initiator  
• Fastest non-temperature-controlled peroxyester                                                                                           |
| *Trigonox 117* | tert-Butyl peroxy-2-ethylhexyl carbonate                      | 6.4               | 98                   | • Excellent intermediate initiator for molding, pultrusion applications                                                                   |
| *Trigonox 127* | tert-Amyl peroxybenzoate                                     | 7.2               | 95                   | • More reactive than tert-butyl analog  
• Reduced cure cycles and residual monomer                                                                                                    |
| *Trigonox 121* | tert-Amyl peroxy-2-ethylhexanoate                            | 6.6               | 95                   | • Pure form, direct sales only                                                                                                              |
| *Trigonox 121-BB75* | tert-Amyl peroxy-2-ethylhexanoate in BBP                    | 5.2               | 75                   | • More reactive and efficient than *Trigonox 21* analog  
• Used in pultrusion and continuous casting applications  
• Temperature-controlled transport and storage                                                                                               |
| *Trigonox 141* | 2,5-Dimethyl-2,5-di(2-ethylhexanoylperoxy) hexane            | 6.7               | 90                   | • Highly reactive intermediate initiator  
• Temperature-controlled transport and storage                                                                                               |
| *Trigonox BPIC-C75* | tert-Butylperoxy isopropyl carbonate                         | 6.8               | 75                   | • Most efficient initiator available for reducing residual monomer in molded FRP parts  
• Can replace tert-butyl peroxybenzoate (TBPB) without sacrificing shelf-life  
• Excellent in food-approved applications                                                                                                     |
| *Trigonox C*   | tert-Butyl peroxybenzoate                                    | 8.0               | 98                   | • Standard initiator in BMC, SMC and pultrusion  
• High purity, stability, low volatility  
• Can be accelerated with metal-based promoters                                                                                               |
### Peroxydicarbonates

<table>
<thead>
<tr>
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<th>Peroxide content (%)</th>
<th>Applications</th>
</tr>
</thead>
</table>
| **Perkadox 16** | Di(4-tert-butylcyclohexyl) peroxydicarbonate, powder | 3.8 | 95 | • Industry standard in pultrusion applications  
• High reactivity (10 hr $t_{1/2} = 40^\circ C$)  
• Fast dissolving in styrene monomer  
• Also useful in continuous casting applications  
• Temperature-controlled transport and storage |

### Peroxyketals

<table>
<thead>
<tr>
<th>Product name</th>
<th>Chemical description</th>
<th>Active Oxygen (%)</th>
<th>Peroxide content (%)</th>
<th>Applications</th>
</tr>
</thead>
</table>
| **Trigonox 22-BB80** | 1,1-Di(tert-butylperoxy)cyclohexane, 80% solution in butyl benzyl phthalate | 9.8 | 80 | • Similar to Trigonox 29-B75  
• Excellent catalyzed shelf-life in BMC and SMC formulations |
| **Trigonox 29-B75** | 1,1-Di(tert-butylperoxy)-3,3,5-trimethylcyclohexane, 75% solution in dibutyl phthalate | 7.9 | 75 | • Highly efficient intermediate initiator  
• Stable in the presence of pigments, especially carbon blacks  
• Can be used with more reactive initiators to achieve reduced cure cycles |
| **Trigonox 122-C80** | 1,1-Di(tert-amylperoxy)cyclohexane, 80% solution in odorless mineral spirits | 8.9 | 80 | • More reactive than Trigonox 22-BB80 |
| **Trigonox KSM** | Mixture of tert-butyl peroxy-2-ethylhexanoate and 1,1-Di(tert-butylperoxy)-3,3,5-trimethylcyclohexane, 75% solution in dibutyl phthalate | 6.1 | 75 | • Complete intermediate/finishing initiator  
• Excellent in BMC, SMC and pultrusion  
• Temperature-controlled transport and storage |
Ambient temperature ranges
Half-life data

1. Perkadox 16
2. Trigonox 141
3. Perkadox L
4. Trigonox 21
5. Trigonox 121
6. Trigonox 29
7. Trigonox 22
8. Trigonox 42
9. Trigonox 97
10. Trigonox BPIC
11. Trigonox 117
12. Trigonox 127
13. Trigonox C
Storage and handling

Storage options

These facilities can carry in size from an isolated storage area in a mixed storage facility such as a warehouse or small quantities within a laboratory to a detached structure dedicated to organic peroxide storage.

Selection of one type over another is based upon three peroxide parameters; the temperature requirements of the product, the violence of decomposition and the quantity. Each category has requirements unique to that designation.

Determining whether or not temperature control is required is a function of the safety temperature of the peroxide(s) in question. If more than one organic peroxide is stored together, the most temperature-sensitive peroxide is the basis for temperature requirements. Ambient storage is considered a viable option if, and only, at no time will the control temperature (available in the product catalog or relevant technical bulletin) be exceeded. If local temperatures can, at any time, exceed the control temperature, temperature control is required. Some products may not require temperature control in order to maintain safety but to maintain quality. Minimal instrumentation and emergency response is acceptable in this case. Temperature control is required for some peroxides according to the guidelines of NFPA 43B.

Some organic peroxides have minimum storage temperatures as well. To prevent the freezing of peroxides, refer to the universal recommendations section for stringent guidelines for heating of the storage area.

Ambient storage

In addition to all of the recommendations outlined in the universal recommendations (see previous section), the area should be:

- *Designated* and *marked* within the warehouse by signs and floor markings at least 25 feet from any incompatible materials or chemicals located along an *exterior wall* or *corner curbed or diked* to isolate peroxide from any incompatible material in storage in the building.
- Not exposed to direct sun, i.e. open loading dock roll-up door(s)
- Selected so as to neither limit nor block an emergency exit in the building away from mail traffic pattern in building
- So as to limit access and exposure to area covered by an automatic sprinkler system (fusible link heads are acceptable)
- Deluge with remote activation is also acceptable
- Remote activation of a manual system is recommended
- Well-ventilated 4 hour, watertight firewall
Temperature controlled storage

Peroxides that require temperature controlled storage are subject to the most rigorous recommendations of any peroxide store. Peroxides can be stored in a cooler or freezer that can be either walk-in or chest-type or in a detached dedicated building.

In addition to all of the universal recommendations temperature controlled storage should have the following features:

- Cooling capacity adequate to maintain the appropriate recommended storage temperature
- Extra cooling
- Electrical classification inside the unit of Class I, Group D, Division I.
- Pre-cooled to a least the control temperature, available from our product catalog or relevant product data sheet, before peroxide is stocked
- Doors or lid should not be locked or bolted closed
- Lids of chest models should close by gravity
- Designated and marked ‘For organic peroxides only’ with the peroxide diamond prominently displayed
- Arrangement of containers such that air is adequately circulated around all containers’
- Temperature monitored with a readout located outside the unit (opening the unit should not be required to read the temperature)
- A monitoring system that will detect a cooling failure and be acknowledged within an adequate period of time to correct the situation (minimum response times determined as a function of the insulation characteristics of actual unit)
- A local alarm signal with a flashing light and audible alarm at the unit and remote signal to a control room
- Alarm set points at the emergency temperature (or below) of the most sensitive peroxide in store
- Insulated with a material that is non-flammable or flame retardant and resistant to the solvents in the products to be stored; polystyrene foam, readily dissolved by aromatic hydrocarbons, is not recommended
Detached storage – additional guidelines

- Buildings must have an individual dedicated cooling unit
- Where possible, install more than one compressor and alternate use so that one is ready as a back-up
- Doors or walls should have no ventilation openings: If fresh air ventilation is desired:
  - Replacement rate should be minimized
  - Outside air intake must not warm up the stored peroxides
  - Moving parts and openings should be protected from ice formation due to ambient humidity
  - Electrical equipment having direct contact with the inside air should be Class I, Group D, Division II.
- Locate cooling units and all other equipments that may generate heat or sparks outside the store and away from the entrance
- Electrical equipment outside the building need to be explosion proof if all wall penetrations are air-tight
- Use cooling agents that are non-flammable and non-reducing: liquid air is not suitable
- Stock ‘spare cold’ like blue ice, dry ice, or the like to slow heat loss during a failure of the cooling unit
- Have emergency power available if the possibility of an electrical main failure exists
- Alarm the cooling unit in case of a failure, to provide the maximum time to correct a problem before peroxide temperature is compromised
- Equip with a temperature monitoring and alarm system and an automatic sprinkler system

Temperature monitoring and alarm system recommendations

- Liquid and air temperature sensors should be inside the building with readout outside and in a control room
- Back-up power should be available for the monitoring and alarm system
- Alarm set points should be based upon the emergency temperature of the most sensitive peroxide in the store with the possibility of short periods of temperature change due to stocking, inventory or the like
- Electrical circuitry of the sensors and the alarms should be independent
- Any possibility of alarm deactivation should be countered with an automatic alarm signal
- Smoke detectors are acceptable for alarm functions only if they are designed for use a low temperatures of the correct electrical classification
- Sensors should activate either flashing lights and/or audible signals, locally and remotely to a control room
- The type of signal is best chosen on the basis of what will insure the most prompt response within the necessary time frame for your facility, including nights, weekends and holidays. An alarm should be treated as a signal to take actions immediately to prevent an undesirable chemical reaction.
• Alarm response depends on the product(s) involved, type of emergency and available resources. For example procedures could include:
  − Area inspection to identify the cause of temperature upset
  − Closing a door that has been left open
  − Starting back-up generator
  − Calling in personnel capable of repairs to either the cooling units, the building itself, or the sensory system
  − Moving product(s) to another store if time to resume cooling is delayed
  − Place dry ice (in blocks or as snow) into the store as a temporary measure while repairs are in progress
  − Alarm systems should be tested before product is loaded

Trigonox, Perkadox, Laurox and Cadox are registered trademarks of Akzo Nobel Chemicals BV or affiliates in one or more territories.
ATTENTION

How to store peroxides

- Observe the recommended storage temperature!
- Store in a cool and dark room
- Leave in the original packaging
- Store in a separate room without accelerators or other chemical substances

How to treat peroxides

- Wear safety goggles
- Wear safety gloves (PVC)
- The use of barrier cream is recommended
- Do not smoke
- Avoid the use of open fire
- Avoid sparking

HOW TO ACT IN CASE OF:

- Fire: Spray liberally with water and alert the fire department
- Spillage: Liquids absorb with inert material
- Solid substance and pastes: absorb as much as possible with a polyethylene spatula and clean the contaminated spot with water
- Skin Contact: Rinse with water and wash with water and soap
- Contact with the eyes: Rinse with running water for at least 15 minutes. Do not treat by any other means. Consult ophthalmologist.
- Ingestion: Drink large quantities of water. Consult doctor.
- Destruction: Contact Akzo Chemicals Inc.