Organic peroxides for PEX-a pipe and tubes

AkzoNobel's range of organic peroxides for the crosslinking of elastomers and thermoplastics is the world's largest, including a number of organic peroxides for the production of PEX-a pipes and tubes. Our products are marketed under the well-known trademark of Trigonox®.

When producing PE pipes and tubes, frequently high density polyethylene (HDPE) is used. To further improve the product properties of HDPE, the polymer matrix is crosslinked to obtain a material denoted as PEX-a. During the crosslinking process, the polyethylene macro-molecules are chemically linked to form a three-dimensional network. This reaction can be achieved by various processes:

- Organic peroxide curing: C-C crosslinks are formed by means of a radical mechanism; the process is a one-step-cure-process (PEX-a).
- Silane cure technology: functional silane groups are grafted onto the polyethylene backbone. In a second step, these reactive groups can further react under influence of a catalyst and water to form crosslinks having a C-Si-O-Si-C structure. This process is a two-step process (PEX-b).
- Electron beam crosslinking, also called radiation cure: C-C crosslinks are formed by applying a separate electron beam process. Also this process is a two-step process (PEX-c).

In this overview, aspects are highlighted for selecting the most suitable organic peroxides for the production of PEX-a pipes and tubes.

Selection of a suitable crosslinking peroxide
From the wide variety of organic peroxides available, only a few are suitable for the crosslinking of high density polyethylene. The major criteria involved are:

- Physical form of the peroxide
- Thermal stability of the peroxide
- Crosslinking ability of the radicals formed
- Environmental, health and safety aspects
- Efficiency.
Physical form
Crosslinkable HDPE compounds can be prepared by different methods. One method consists of absorption of the peroxide by the polyethylene powder by means of long term soaking. This technique requires a liquid version of the peroxide to guarantee optimal dispersion/absorption of the peroxide into the polymer phase.

Thermal stability
Since crosslinkable HDPE is processed in the molten phase, and given the fact that during this processing premature crosslinking (gelation) must be prevented, only the most thermally stable organic peroxides can be used. However, the peroxide should still be reactive enough to prevent the need for an excessively high cure temperature and/or long cure time.

Suitable radicals
Only peroxides that decompose into radicals, with the ability to abstract secondary and tertiary hydrogen atoms from the polyethylene backbone, can be used in this application. These peroxides can generate polymer radicals which can react to form C-C crosslinks. Mainly peroxides generating methyl- and tert-butoxy radicals are applied in the crosslinking process of HDPE.

Environmental, Health and Safety (EH&S) aspects
Peroxides to be selected for HDPE crosslinking should be in line with the applicable EH&S regulations and recommendations and should be safe during production, transport, storage and handling. Peroxides selected for the PEX-a production process belong to the most thermal stable classes of organic peroxides, so that cooling during transport or storage is not required. For quality reasons (assay) the recommended storage temperature is usually max. 30°C. Besides safety features, environmental and health aspects should also meet the standards set for production and final use of PEX-a articles. Not only the peroxide as such, but also the peroxide decomposition products and potentially formed adducts, have to be taken into account. Safety and toxicity properties can be found in the appropriate Material Safety Data Sheets (MSDS) which can be downloaded from www.akzonobel.com/polymer.

Efficiency
Efficiency of organic peroxides not only depends on the type of peroxide and the radicals formed, but also on the efficiency of the reaction steps involved (peroxide decomposition, hydrogen abstraction and combination of polymer radicals) and the susceptibility of the polymer towards crosslinking. Furthermore it should be realized that the crosslink efficiency can be negatively impacted by side reactions such as β-scission of the polymer radicals. Additionally, certain compound additives such as antioxidants may show excessive free radical scavenging activity. It is therefore recommended to contact raw materials suppliers to select the correct HDPE grade and the optimal protection system.

Based upon the above mentioned criteria, AkzoNobel is supplying three key organic peroxides for the production of PEX-a pipes and tubes: Trigonox B, Trigonox 145-E85 and Trigonox 311.
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Features of the individual peroxides:

**Trigonox B**
Chemical name: Di-tert-butyl peroxide

**Properties:**
- Colorless liquid at room temperature, assay > 99%
- Very high thermal stability; safe processing guaranteed without premature cure at temperatures up to 145°C
- Recommended dosage level for HDPE: 0.3 – 0.6%
- Product on positive list for drinking water application (Germany, The Netherlands)
- The relatively high volatility in combination with very low flashpoint (6°C) and sensitivity for static electricity demand correct safety precautions!
- Mainly applied in closed systems such as “ram-extrusion-process”. Trigonox B should not be used in open systems like IR-curing lines!
- Major decomposition products; methane, acetone and tert-butanol
- Di-tert-butyl peroxide is currently classified at EU-level as a mutagen; possible risk of irreversible effects.

**Trigonox 145-E85**
Chemical name: 2,5-dimethyl-2,5-di(tert-butylperoxy)hexyne-3

**Properties:**
- Colorless solution in mineral oil at room temperature, assay 85%
- Very high thermal stability; safe processing guaranteed without premature cure at temperatures up to 145°C
- Recommended dosage level for HDPE: 0.5 – 1.2%
- Product on positive list for drinking water application (Germany, The Netherlands)
- Major decomposition products; methane, acetone, tert-butanol and 2,5-dimethyl-3-hexyn-2,5-diol
- Blooming might occur from one of the decomposition products after crosslinking
- Mainly applied in systems such as the double screw extrusion process; possible to use in combination with IR-curing technology
- Product recommended as replacement for Trigonox B.

**Trigonox 311**
Chemical name: 3,3,5,7,7-pentamethyl-1,2,4 trioxepane

**Properties:**
- Colorless liquid at room temperature, assay >95%
- Extremely high thermal stability; safe processing guaranteed without premature cure at temperatures up to 170°C. This peroxide allows for a much wider processing window or the use of new extrusion technology (crosshead die)
- Recommended dosage level for HDPE: 0.35 – 1.2%
- Major decomposition products: methane, acetone, isopropyl acetate, 3-hydroxy-1,3 dimethylbutyl acetate, 3-methoxy-1,3-dimethylbutyl acetate. (No tert-butanol!)
- Product has characteristic smell
- Product intended for single and double screw extrusion application followed by IR-cure technology
- Cure kinetics (temperature and time) needs to be evaluated very well, product cannot be considered as ‘drop-in’ for Trigonox B and/or Trigonox 145-E85.
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Hole in one with Perkadox® and Trigonox® cross-linking peroxides

Running a successful business is like playing golf. To maximize performance and create competitive advantage, you need the very best materials.

If you’re in the business of crosslinking elastomers and thermoplastics, then our Perkadox and Trigonox organic peroxide brands are at the top of the leader board.

www.akzonobel.com/polymer

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