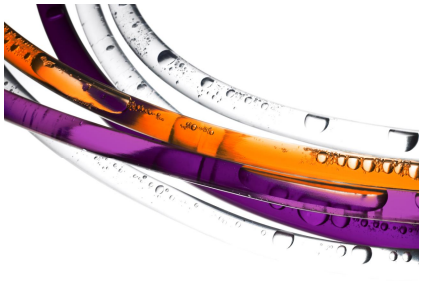
Organic peroxides for PEX-a pipes and tubes

AkzoNobel
Tomorrow's Answers Today



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 PEX pipes and tubes, high density polyethylene (HDPE) is used. To further improve the product properties of HDPE, the polymer matrix can be crosslinked. 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 (PEX-b)
- Electron beam crosslinking, also called radiation cure: C-C crosslinks are formed by applying a separate electron beam process (PEX-c).

In this overview, aspects are highlighted for selecting the best 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 by means of long term soaking. A second group of techniques involves direct blending/dosing of the peroxide into the polymer, just before the extrusion operation. Both techniques require a liquid version of the peroxide to guarantee optimal dispersion of the peroxide in 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 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 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). Furthermore, the crosslink efficiency can be negatively impacted by side reactions such as ß-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 the newly developed Trigonox 311.

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 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
- 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.

Current status and outlook

Over the last few years, the PEX-a industry has faced several new technologies. New production requirements such as longer production runs and higher line speed in combination with novel pipe design, has triggered new developments. It has brought equipment producers and raw material suppliers together to work on one step multi-layer pipe production, improved IR-heating technology, 'single-stage production process' and other concepts.

Consequently, polymer producers introduced new products, e.g. Borealis developed BorPEX HE1878E-C2 - a special HDPE grade, requiring only the addition of an organic peroxide; Inoex, a supplier of complete PEX-a production lines, introduced a new mixer and dosing equipment - the 'SAVEOMAT' (multi component dosing station), which is able to produce a well dispersed blend of solids (polymer and stabilizer) and the liquid peroxide.

New production technologies also demanded a search for safer and more robust organic peroxides. Beside the standard crosslinking peroxides such as Trigonox B, AkzoNobel also provides a more suitable and safer 'drop-in' peroxide: Trigonox 145-E85.

In addition, Trigonox 311, a peroxide with an extremely high thermal stability, allowing significantly more freedom during the extrusion process of HDPE-compounds has been introduced for the production of PEX-a pipes and tubes. On average, 20 - 30°C higher melting temperatures can be applied with the use of Trigonox 311 compared to the standard peroxides used in this application.

As a company of innovation, we believe the only way to grow is by developing sustainable, innovative solutions that benefit our customers. Much of our success is due to our philosophy of creating close partnerships with our customers and other technology providers. We share our experience and are committed to your success.

For more information

Americas
AkzoNobel Functional Chemicals
525 West Van Buren Street
Chicago, IL 60607
United States
T +1 800 828 7929 (US only)
T +1 312 544 7000
F +1 312 544 7188
E polymerchemicals.na@akzonobel.com

Asia Pacific
Akzo Nobel (Asia) Co. Ltd.
The Exchange, 5th Floor
299 Tong Ren Road
Shanghai 200040
P.R. China
T +86 21 2216 3600
F +86 21 3360 7739
E polymerchemicals.ap@akzonobel.com

Europe, Middle East and Africa
AkzoNobel Functional Chemicals
Stationsstraat 77
P.O. Box 247
3800 AE Amersfoort
T +31 33 467 6767
F +31 33 467 6100
E polymerchemicals.nl@akzonobel.com

www.akzonobel.com/polymer

AkzoNobel is the largest global paints and coatings company and a major producer of specialty chemicals. We supply industries worldwide with innovative products and are passionate about developing sustainable answers for our customers. Our portfolio includes well known brands such as Armostat, Ketjenblack, Perkadox, Trigonox, Sikkens and Eka. Headquartered in Amsterdam, the Netherlands, we are a Global Fortune 500 company and are consistently ranked as on e of the leaders on the Dow Jones Sustainability Indexes. With operations in more than 80 countries, our 55,000 people around the world are committed to excellence and delivering Tomorrow's Answers Today ™.