# CROSSLINKING of rubber and polyolefines with organic peroxides





# PERGAN The Peroxide Company

Reliable, competent, flexible - for 35 years your partner for organic peroxides. Since its foundation in 1981, Pergan has established itself in the national and international market as a manufacturer of organic peroxides.

Our business activities are conducted from two production facilities in Germany, one production facility in the United States, through a network of more than 30 representatives worldwide and a joint venture company in China. We foster constructive and trusting business connections with our national and international partners.

## **Organic peroxides**

The main stress of our business activity is put on the production and trade of organic peroxides. These are more or less stable chemical compounds which exclusively consist of carbon, hydrogen and oxygen. They are used as initiators and reaction substances in the plastics and rubber industry, because they easily decay in extremely active radicals.



#### Organic peroxides are used for:

- polymerization of monomers for plastics manufacture
- crosslinking and modification of polymers,
- as the curing of unsaturated polyester-, vinylester- and acrylic resins

Organic peroxides are furthermore used as oxidation materials for medical preparations and for complicated chemical synthesis.

#### Safety and environmental conservation out of responsibility

Organic peroxides are highly reactive chemicals. The manufacturing, transport, storage, handling and last but not least the disposal of organic peroxides requires strict precautions. We have effected considerable investments into

safety to eliminate risks, to avoid faults and to protect people and environment from becoming endangered. Naturally, we provide our customers support in any kind of safety, handling, or storage issue.

# Customer orientation – a recipe for success

#### Reliable

Quality does not only mean reliability but also includes services such as consultation and support for our customers helping them to solve their problems. Quality results from the performance of all employees. We work towards strengthening quality awareness through the help of information, internal and external training and motivation.

#### Competent

Part of our service also includes examining our customers' applications so that we can develop optimal product formulations and supply them with suitable peroxide- and other additive preparations for their process. Therefore we do not offer only products but moreover solutions to problems. The positive feedback from satisfied customers motivates us to keep continuing along this line.



and ISO 14001 certification

#### Flexible

As a medium sized company flexibility is one of our greatest strengths. We are able to react quickly, competently and efficiently to the individual wishes and requirements of our customers. In recognition of exceptional business achievements PERGAN was awarded the jury award "Company of the Year 2010" by Stadtsparkasse Bocholt.



# CROSSLINKING

# of rubber and polyolefins with organic peroxides

Chemical crosslinking agents such as sulphur and organic peroxides are able to link polymer chains creating a three-dimensional network. This crosslinking reaction changes several material characteristics. The material characteristics of a crosslinked polymer are superior to the equivalent characteristics of the sulphur cured polymers.

# Peroxide crosslinking of elastomers has the following advantages over the sulphur cure:

- simple formulation
- long storage time of the peroxide containing compound without scorching
- high processing temperature
- rapid vulcanization without reversion
- high temperature resistance of final product
- crosslinked products do not change colour through contacts with metals and PVC
- most peroxides do not cause blooming
- co-vulcanization of saturated and unsaturated rubbers
- co-vulcanization of rubbers with polyethylene and other polyolefins
- co-polymerisation with polymerisable plasticisers or other co-agents to achieve a controlled hardness and stiffness coupled with easy processing

## In comparison to sulphur cure there are following disadvantages:

- sensitivity to oxygen under curing conditions
- certain components of the rubber compound like extender oils, antioxidants and resins may consume peroxide free radicals under certain conditions
- $\bullet \;\;$  usually tensile and tear strength properties are reduced by 15%

#### Peroxide crosslinking possible for:

NR	Natural rubber	EPDM	Ethylene propylene terpolymer
IR	Polyisoprene rubber	POE	Polyolefi n elastomer
BR	Polybutadiene rubber	Т	Polysulphite rubber
CR	Polychloroprene rubber	PE	Polyethylene
SBR	Styrene butadiene rubber	CM	Chlorinated Polyethylene
NBR	Butadiene acrylonitrile rubber	CSM	Chlorosulphonyl polyethylene
HNBR	Hydrogenated butadiene acrylonitrile rubber	ABS	Acrylonitrile butadiene styrene copolymer
Q	Silicone rubber	EVA	Ethylene vinylacetate copolymer
AO/EO	Polyurethane rubber	EBA	Ethylene butylacrylate copolymer
EPM	Ethylene propylene copolymer	FPM	Fluoro rubber

#### Peroxide crosslinking possible with blends of:

NBR / EPDM	SBR / EPDM	PE / EPDM	PE / EVA
NBR / EVA	EPDM / PP	POE / EP(D)M	

#### Peroxide crosslinking limited or impossible for:

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

#### Peroxide formulation with improved scorch protection

**PEROXAN BIB-40 GS+** is a new product which offers improved scorch protection as compared to **PEROXAN BIB-40 GS**. It offers significantly better scorch protection during mixing and compounding which results in increased productivity.

#### Advantages during mixing:

- increased mixing speeds which result in shorter mixing times
- makes one step mixing a possibility
- improves the dispersibility of components

#### Advantages during processing:

- higher processing temperatures which results in shorter cycle times
- faster filling of moulds
- higher speeds during the extrusion process

#### Azo-Initiators as a blowing agent

**PEROXAN AZDN-Paste 50 SI** is used as a chemical blowing agent for the production of silicone foams and other expanded elastomeric products. When 2,2'-Azodiisobutyronitril decomposes it releases Nitrogen gas and forms a homogeneous sponge structure within the elastomer. The physical form as a paste facilitates the dust-free incorporation into silicone rubber and other low viscous elastomeric compounds.

## Typical amounts of organic peroxides required for crosslinking of various polymers

Additions of the important peroxides for the crosslinking of different types of polymers are listed on the next page. Satisfactory mechanical properties can be obtained at the lowest peroxide dosage levels. Compression set properties improve with higher peroxide amounts. The highest values should not be surpassed, otherwise the remaining mechanical properties will decrease. However, higher peroxide levels are necessary when the compound contains free radical consuming materials such as sulphur, certain antioxidants and non-paraffinic mineral extender oils.

	Par	ts of peroxide per	100 parts of poly	mer	
Polymer	PEROXAN PK295 P	PEROXAN BV-40 P	PEROXAN DC-40 P	PEROXAN BIB-40 P	PEROXAN HX-45 P
NR, IR	2,3 - 4,5	2,5 - 5,0	2,0 - 4,1	1,3 - 2,5	1,3 - 2,4
BR	1,0 - 2,1	1,1 - 2,3	0,9 - 1,9	0,5 - 1,2	0,8 - 1,2
CR	1,1 - 3,0	1,3 - 3,3	1,0 - 2,7	0,6 - 1,7	0,6 - 1,6
SBR	1,9 - 4,1	2,1 - 4,6	1,7 - 3,7	1,1 - 2,3	1,1 - 2,2
NBR	2,6 - 4,5	2,9 - 5,0	2,4 - 4,1	1,5 - 2,5	1,4 - 2,4
HNBR	6,8 - 11,3	7,5 - 12,5	6,1 - 10,1	3,8 - 6,3	3,7 - 6,1
EPM, EPDM	6,8 - 11,3	7,5 - 12,5	6,1 - 10,1	3,8 - 6,3	3,7 - 6,1
PE	1,5 - 7,6	1,7 - 8,4	1,4 - 6,8	0,8 - 4,2	0,8 - 4,0
CM	6,8 - 10,6	7,5 - 11,7	6,1 - 9,5	3,8 - 5,9	3,7 - 5,7
EVA	2,6 - 5,3	2,9 - 5,8	2,4 - 4,7	1,5 - 3,0	1,4 - 2,9
Q			1,0 - 2,0	0,4 - 0,8	0,4 - 0,8
t90 Crosslinking*	145°C	160°C	170°C	175°C	175°C
t2 Crosslinking	115°C	125°C	130°C	135°C	135°C

<sup>\*</sup> Very short crosslinking times can be achieved by raising t90- temperatures to approximately 40°C above the mentioned temperature.

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# **APPLICATIONS**

#### **Cable insulation**

Cable insulation from peroxide cross-linked polyethylene (XLPE) are used in 1-380 kV range. Important after crosslinking are good dielectric properties and dimensional stability at higher temperatures. Mostly LDPE is crosslinked with Dialkylperoxides.

#### NBR & SBR

Butadiene acrylonitrile rubber (NBR) is produced by copolymerization of acrylonitrile (ACN) and 1,3-butadiene. Materials based on this synthetic rubber are suitable because of their good technological properties for many applications. In particular, radial shaft seals, sealing elements for hydraulic and pneumatic systems as well as O-rings.

Styrene butadiene rubber (SBR) is produced by the copolymerization of 1,3-butadiene and styrene. SBR is now the most widely used synthetic rubber and finds its application in the production of tires (tread), gaskets and conveyor belts.

#### **Crosslinked Foamed Polyethylene**

Crosslinked polyethylene foam is produced by crosslinking of polyethylene in the presence of foaming agents, such as e.g. Azo initiators. Crosslinked PE foam has a fine, regular and closed cell structure with low density. The closed cell structure provides excellent heat and cold insulation properties. In addition, cross-linked PE foam does not absorb water. Applications are noise protection, thermal insulation, seat cushions, gym mats or floats (swimming aids).

#### **Crosslinked EVA**

Ethylene vinyl acetate (EVA) is a class of copolymers. The crosslinking with organic peroxides is carried out in order to improve the elongation, the aging and the heat resistance. Applications are hot melt adhesives, films, electrical cables, solar panels, shoe soles and floor coverings.

#### Crosslinked EPM/EPDM

Ethylene-propylene copolymer (EPM) is a copolymer of ethylene and propylene, ethylene-propylene terpolymer (EPDM) is a terpolymer of ethylene, propylene and a diene component. Advantages are more enhanced temperature resistance, lower compression set and a better aging behavior. Applications are hoses, seals, profiles, cables, shoe soles and conveyor belts.

#### Crosslinked HDPE & Crosslinked LDPE

Crosslinked Polyethylene (PE-X) is produced by crosslinking of thermoplastic polyethylene (LDPE, LLDPE or HDPE) through organic peroxides. Due to the crosslinking the impact resistance, abrasion resistance, low-temperature and stress cracking resistance can significantly be increased. On the contrary the hardness and rigidity decreases. As PE-X does not melt it is more thermally resistant. With a higher crosslinking density the maximum shear modulus increases also. Crosslinking of PE is only applied to the finished or semi-finished product. Applications are rotationally sintered hollow bodies, underfloor heating pipes, medium and high voltage cable insulation or container linings.

#### **Crosslinked Silicone Rubber**

Silicones (poly (organo) siloxanes) is a group of synthetic polymers in which silicon atoms are linked via oxygen atoms. As silicone rubber is referred to the compositions of the poly (organo) siloxanes transferred into a rubber-elastic state. Silicone rubber differs in two types according to the required curing temperature: a cold- (RTV) and a hot-crosslinked (HTV) silicone rubber. Both types can, in addition to the silane or platinum crosslinking, be crosslinked with organic peroxides. Crosslinked silicone rubber has a good cold-/heat- and aging resistance and can be used for hoses, rollers, conveyor belts, cable sheathing, gaskets and for pharmaceutical and medical products. As crosslinkers we recommend our peroxide formulations based on silicone oil or silicone rubber.

### Safe processing- and crosslinking times

#### Safe processing temperature t2

The raw materials (polymer, additives, peroxide) have to be homogenized before the crosslinking reaction can take place. Although the temperature sensitive peroxide will be the last raw material which is added for homogenization, one has to take care to avoid temperatures at which the peroxide decomposes and the crosslinking reaction starts. This maximum processing temperature of the peroxides is called the scorch temperature. The safe processing temperature t2 is defined as the temperature, at which the scorch time is longer than 20 minutes.

#### Typical crosslinking temperature t90

The typical crosslinking temperature t90 is defined as the temperature at which 90% of the crosslinks in the compound are formed within about 12 minutes.

#### Storage temperatures

Crosslinking peroxides can be stored and handled without risk providing certain precautions are taken. Please refer to our MSDS and product labels for precise information and keep products at recommended storage temperature.

PEROXAN BD	°C	70	80	90	100	110	120	130	140	150	160	170	180	190	200
Safe processing time	min	47	12	2											
Crosslinking time	min			10	4	2									
PEROXAN PB															
Safe processing time	min			29	20	11									
Crosslinking time	min						61	30	12	5					
PEROXAN PK295															
Safe processing time	min					35	11								
Crosslinking time	min							50	16	7					
PEROXAN BV															
Safe processing time	min						35	12							
Crosslinking time	min								72	30	11	5			
PEROXAN DC															
Safe processing time	min						77	24							
Crosslinking time	min									65	25	10	4		
PEROXAN BIB															
Safe processing time	min							58	19						
Crosslinking time	min										46	22	7	3	
PEROXAN BU															
Safe processing time	min							57	19						
Crosslinking time	min										46	19	6	3	
PEROXAN HX															
Safe processing time	min							45	15						
Crosslinking time	min										60	24	8	3	
PEROXAN DB															
Safe processing time	min								54	18					
Crosslinking time	min										86	34	12	5	2
PEROXAN HXY															
Safe processing time	min								43	14					
Crosslinking time	min											63	22	8	4

Trade name	Chemical name / Chemical structure	CAS number / Physical form	Peroxide assay	Active oxygen assay	Standard package	Storage temperatures max. min		Half life temperature 1h	e <b>s</b> 0,1h	Proces tempera t2		Regula Recommen FDA		UN- No.
	Di-(2,4-dichlorobenzoyl)-peroxide	133-14-2					47°C	65°C	80°C	75°C	90°C			
PEROXAN BD-Paste 50 SI	CI- CI CI CI	Paste in silicone oil	50%	2,11%	20kg pail	30°C 5°C						177.2600	XV	3106
	tert-Butyl peroxybenzoate	614-45-9					87°C	110°C	136°C	100°C	140°C			
PEROXAN PB PEROXAN PB-50 P	CH <sub>3</sub> O CH <sub>3</sub> —C—O—O—C—	Liquid Powder with chalk	98% 50%	8,07% 4,12%	25kg container 25kg cardboard box	30°C 10°C 30°C							XLVI	3103 3106
	1,1-Di-(tert-butylperoxy)-3,3,5-trimethylcyclohexane	6731-36-8					91°C	117°C	138°C	115°C	145°C			
PEROXAN PK295 P PEROXAN PK295 GS PEROXAN PK295 MB	CH <sub>3</sub>	Powder with chalk Granules with chalk Granules with EPM	40% 40% 40%	4,23% 4,23% 4,23%	25kg cardboard box 25kg cardboard box 25kg cardboard box	30°C 30°C								3110 3110 3110
	Butyl-4,4-di-(tert-butylperoxy) valerate	995-33-5					104°C	130°C	152°C	125°C	160°C			
PEROXAN BV-40 P PEROXAN BV-40 GS	CH <sub>3</sub> O CH <sub>3</sub>	Powder with chalk Granules with chalk	40% 40%	3,83% 3,83%	25kg cardboard box 25kg cardboard box	30°C 30°C								3108 3108
	Dicumyl peroxide	80-43-3					112°C	138°C	162°C	130°C	170°C			
PEROXAN DC PEROXAN DC-P PEROXAN DC-P+ PEROXAN DC-Paste 50 SI/3 PEROXAN DC-40 GS PEROXAN DC-40 MB PEROXAN DC-40 PE-G PEROXAN DC-40 PK PEROXAN DC-40 P PEROXAN DC-20 PE-MB	CH <sub>3</sub> CH <sub>3</sub> C-0-0-C  CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>	Fine granules Powder Powder Paste in silicone oil Granules with chalk Granules with EPM Granules with PE Powder with clay Powder with chalk Masterbatch with PE	98% 98% 98% 50% 40% 40% 40% 40% 20%	5,80% 5,80% 5,80% 2,96% 2,37% 2,37% 2,37% 2,37% 2,37%	20kg cardboard box 20kg cardboard box 20kg cardboard box 25kg pail 25kg cardboard box 25kg cardboard box 20kg cardboard box 20kg cardboard box 25kg cardboard box 25kg cardboard box 20kg cardboard box	30°C 30°C 30°C 30°C 30°C 30°C 30°C 30°C						177.2600	XV, XXXIX	3110 3110 3110 3110 3077 3077 3077 3077

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Trade name	Chemical name / Chemical structure	CAS number / Physical form	Peroxide assay	Active oxygen assay	Standard package	Stor temper max.		10h	Half life emperature	<b>s</b> 0,1h		essing ratures t90	Regul Recomme FDA		UN- No.
	Di-(2-tert-butyl-peroxyisopropyl)-benzene	25155-25-3						117°C	146°C	169°C	135°C	175°C			
PEROXAN BIB-1 PEROXAN BIB-40 EV-G PEROXAN BIB-40 GS PEROXAN BIB-40 GS+ PEROXAN BIB-40 MB PEROXAN BIB-40 PE-G PEROXAN BIB-40 PK PEROXAN BIB-40 P	CH <sub>3</sub>	Powder Granules with EVA Granules with chalk Granules with chalk Granules with EPM Granules with PE Powder with clay Powder with chalk	95% 40% 40% 40% 40% 40% 40%	8,98% 3,78% 3,78% 3,78% 3,78% 3,78% 3,78%	20kg cardboard box 20kg cardboard box 25kg cardboard box 25kg cardboard box 25kg cardboard box 20kg cardboard box 20kg cardboard box 20kg cardboard box	30°C 30°C 30°C 30°C 30°C 30°C 30°C								XXXIX, XLVI, XXI	3106 none none none none none none
	tert-Butylcumylperoxide	3457-61-2						117°C	146°C	169°C	135°C	175°C			
PEROXAN BU	CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> —C—O—O—C— CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>	Liquid	94%	7,22%	25kg container	30°C	15°C							XV	3107
	2,5-Dimethyl-2,5-di-(tert-butylperoxy)-hexane	78-63-7						118°C	147°C	171°C	135°C	175°C			
PEROXAN HX PEROXAN HX-Paste 75 SI PEROXAN HX-Paste 70 SH PEROXAN HX-50 PS PEROXAN HX-Paste 45 SI PEROXAN HX-45 SP PEROXAN HX-45 GS PEROXAN HX-45 MB PEROXAN HX-45 P PEROXAN HX-45 TA	CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> —C—O—O—C—CH <sub>2</sub> —CH <sub>2</sub> —C—O—O—C—CH <sub>3</sub> I CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>	Liquid Paste in silicone oil Paste with fillers Powder with silica Paste in silicone oil Paste in silicone rubber Granules with chalk Granules with EPM Powder with chalk Powder with chalk and TAIC	92% 75% 70% 50% 45% 45% 45% 45% 45%	10,14% 8,27% 7,71% 5,51% 4,96% 4,96% 4,96% 4,96% 4,96% 2,87%	25kg container 25kg pail 25kg pail 25kg cardboard box 25kg pail 18kg pail 25kg cardboard box 25kg cardboard box 20kg cardboard box 25kg cardboard box	40°C 40°C 40°C 40°C 40°C 40°C 40°C 40°C 40°C 40°C	10°C 10°C 10°C 10°C 10°C 10°C						177.2600	XV, XXXV, XLVI	3103 3108 3108 3108 3108 3108 3108 3108
	Di-tert-butylperoxide	110-05-4						120°C	154°C	176°C	145°C	180°C			
PEROXAN DB	CH <sub>3</sub>	Liquid	98%	10,72%	20kg container	40°C							177.2600	XXXV, XLVI	3107
	2,5-Dimethyl-2,5-di(tert-butylperoxy)hexyne-3	1068-27-5						127°C	157°C	182°C	145°C	185°C			
PEROXAN HXY-85 W PEROXAN HXY-45 P	CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> C—O—O—C—C—C—C—O—O—C—CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>	Solution in white oil Powder with chalk	85% 45%	9,50% 5,03%	25kg container 25kg cardboard box	30°C	10°C							XLVI	3103 3106
Blowing agent	2,2'-Azodiisobutyronitril	78-67-1		Assay				Applicat	tion						
PEROXAN AZDN-Paste 50 SI	CH <sub>3</sub> CH <sub>3</sub>	Paste in silicone oil		50%	25kg pail	20°C		of silicon	AN AZDN-Pa e foams. The ation into silic	physical fo	orm as a past		e production the dust-free		3234





710 Bussey Rd Marshall, TX 75670 USA

T +1 903-938-5141 info@perganmarshall.com



#### PERGAN GmbH

Schlavenhorst 71 46395 Bocholt Germany

T +49 (0) 2871 / 99 02-0 F +49 (0) 2871 / 99 02-50 sales@pergan.com



#### PERGAN Fine Chemical Co. Ltd.

Maotiao Road, Nanhe Industrial Zone Tianjin, 300382 P.R. China

> T +86-22-23982200 F +86-22-23983300 yeekew@yahoo.com