

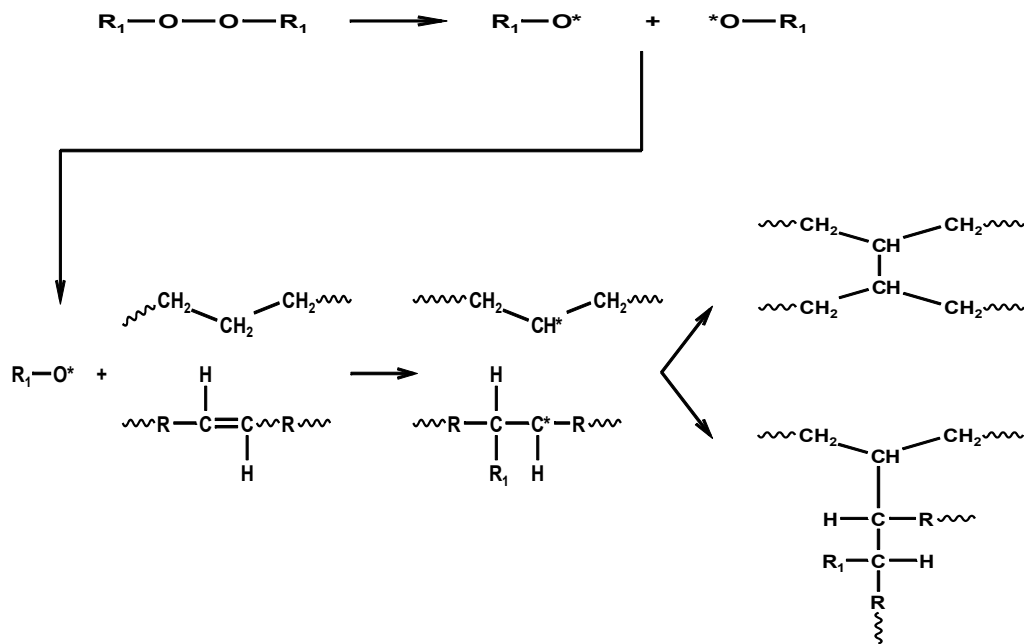
Crosslinking of rubbers and polyolefines

with Organic Peroxides

Introduction

Chemical crosslinking agents such as Sulphur or Organic Peroxides are able at appropriate processing conditions to chemically link polymer chains forming a three-dimensional network (Figure 1).

Figure 1: Crosslinking Process of Rubber



This crosslinking reaction changes several material characteristics. The material characteristics of a crosslinked polymer will be superior to the equivalent characteristics of the non-crosslinked raw materials.

The classical crosslinking agents like Sulphur or Sulphur liberating agents are only effective for unsaturated polymers, i. e. polymers with a C=C double bond (like EPDM). Due to historical reasons this reaction is named *Vulcanization*. The name Crosslinking characterizes the crosslinking reaction of polymers/elastomers initiated by organic peroxides. Besides there exists a crosslinking reaction, which is initiated by high energy radiation, e. g. electron or γ radiation.

Table 1: Polymers/Elastomers Suitable/Not-Suitable for Crosslinking with Organic Peroxides

Organic Peroxide Crosslinking is possible for:	<ul style="list-style-type: none"> • NR Natural Rubber • IR Polyisoprene Rubber • BR Polybutadiene Rubber • CR Polychloroprene Rubber • SBR Styrene Butadiene Rubber • NBR Butadiene Acrylonitrile Rubber • HNBR Hydrogenated NBR • Q Silicone Rubber • AO/EO Polyurethane Rubber • EPM Ethylene Propylene Copolymer • EDPM Ethylene Propylene Terpolymer • POE Polyolefin Elastomer • T Polysulphite Rubber • PE Polyethylene (LDPE and HDPE) • CM Chlorinated PE • CSM Chlorosulphonyl PE • EVA Ethylene Vinylacetate Copolymer • ABS Acrylonitrile Butadiene Styrene Copolymer • EBA Ethylene Butylacrylate Copolymer • FPM Fluoro Rubber
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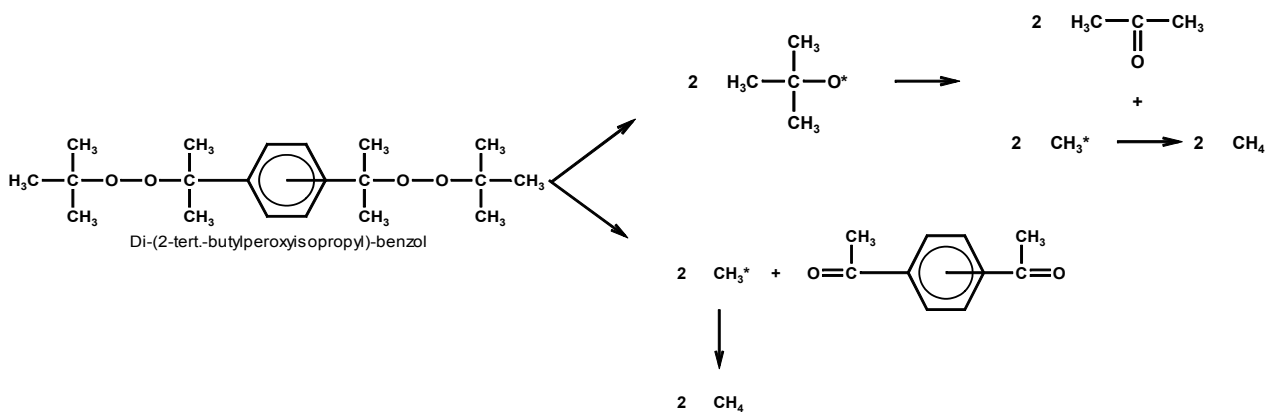
Organic Peroxide Crosslinking is possible with Blends of:	<ul style="list-style-type: none"> • NBR/EPDM • SBR/EPDM • PE/EPDM • PE/EVA • NBR/EVA • EPDM/PP • POE/EP(D)M
Organic Peroxide Crosslinking is limited or impossible for:	<ul style="list-style-type: none"> • ACM Polyacrylate Rubber • IIR Butyl Rubber • CIIR Chlorobutyl Rubber • CO Epichlorhydrin Rubber • ECO Epichlorhydrin Copolymer • PP Polypropylene • PB Polybutylene-1 • PIB Polyisobutylene • PVC Polyvinylchloride

Crosslinking with Organic Peroxides

The crosslinking reaction links linear or branched macromolecules by C-C single bonds. The basic difference with respect to the free-radical polymerisation induced by organic peroxides is that the crosslinking reaction is a *stoichiometric reaction*. That means doubling the peroxide dosage results in a doubling of the number of C-C links. Only Organic Peroxides which decompose in high energy radicals can abstract a hydrogen atom from the polymer molecule and induce a crosslinking reaction. This limits the number of Organic Peroxides which can be utilized for crosslinking of Polymers/Elastomers drastically.

The hydrogen abstraction is performed by a radical formed by a temperature induced decomposition of the organic peroxide. This radical will abstract the hydrogen atom either directly (*primary decomposition*), or the original formed radical continues decomposition by generating a not reactive molecule and a new radical performing the hydrogen abstraction (*secondary decomposition*).

Figure 2: Primary and Secondary Decomposition of Peroxides into Radicals



Improvements of Mechanical and Chemical Properties of Crosslinked Polyolefins/Elastomers

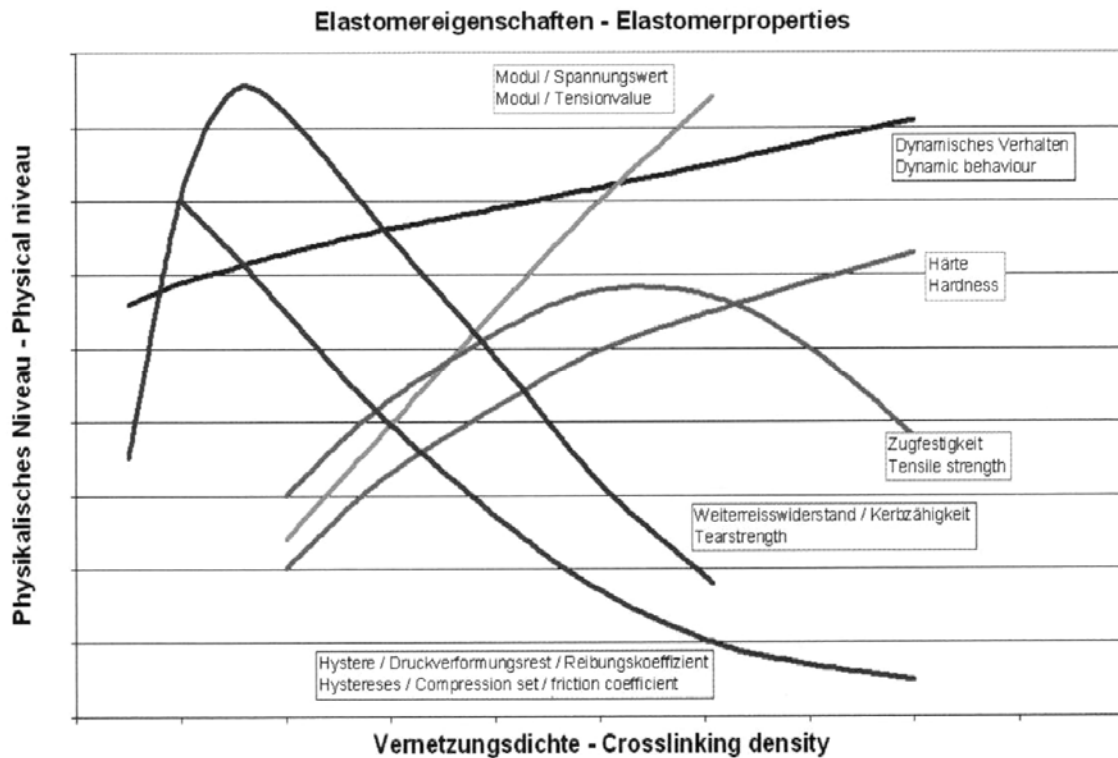
The in table 2 listed properties are improved by crosslinking.

Table 2: Improved Properties of Polymers/Elastomers by the Crosslinking

• Stress and Elastic Modulus	• Compression Set
• Permanent Elongation	• Stress Crack Resistance
• Abrasion Resistance	• Temperature Resistance
• Chemical Resistance	• Ageing Resistance
• Electrical Insulation	• Gas Impermeability

It is important to know that optimal properties of the final crosslinked products are not always obtained at the highest achievable degree of crosslinking (Figure: 3).

Figure 3: Properties affected by the Crosslinking Process



Comparison Vulcanisation – Crosslinking with Organic Peroxides

In table 3 we will have a closer look at the advantages and disadvantages of crosslinking with organic peroxides.

Table 3: Comparison Vulcanisation – Crosslinking with Organic Peroxides

Advantages:

- Organic Peroxides can be utilized for crosslinking of unsaturated and saturated polymers/elastomers. *Vulcanisation is only possible for unsaturated polymers/elastomers.*
- Copolymerisation of Elastomers with PE and other Polyolefines as well as with polymerisable additives in the compound (e.g. certain plasticisers) is possible.
- Peroxidic crosslinked polymers/elastomers have superior mechanical and physical properties, a better resistance to temperature, oxidation, ageing and stress crack corrosion, a brighter colour and are not sensitive to discolouring while in contact with metals or PVC.
- Simple compound formulation; long shelf life of the Organic Peroxides containing compound.
- High processing temperatures possible; fast crosslinking reaction without reversion.
- Most Organic Peroxides do not cause blooming in the final products.
- Use of Coagents allows achieving a controlled hardness and stiffness, coupled with an easy processing.

Disadvantages:

- Crosslinking reaction induced by Organic Peroxides can be inhibited at outer surfaces of crosslinked parts by Oxygen of ambient air.
- Certain additives in the compound, such as extender oils, antioxidants and pigments may consume peroxidic radicals.
- Crosslinking time can only be lowered while increasing reaction temperature
Vulcanisation time can be accelerated by several chemical additives.
- Usually tensile and tear strength are slightly reduced.

Applications for Crosslinking Polyolefins/Elastomers by Organic Peroxides

Organic peroxides are used for the crosslinking in the applications which are listed in table 4.

Table 4: Applications for Crosslinking Polyolefins/Elastomers by Organic Peroxides

Cable (Electric) Insulation:	crosslinked LDPE (up to voltage of 380 kV); EPM/EPDM (lower voltage)
Pipes (Water, Underfloor Heater, Offshore):	crosslinked LDPE and HDPE
Parts made by Rotational Moulding/ Rotational Sinter Process (e. g. IBC):	crosslinked EVA, LDPE and HDPE (Sinter Process)
Foamed Parts with Closed-Cell Structure:	crosslinked and foamed LDPE and EVA and other Polymers/Elastomers (thermal/noise insulation, upholsteries, shoe soles)
Profiles/Seals (e. g. Car Industry):	mainly crosslinked EPM/EPDM
Roller Coverings/Conveyor Belts/ Tubes:	crosslinked EPM/EPDM, NBR, Silicone Rubber and other Polymers/Elastomers
Medical/Pharmaceutical Products, Car Industry (e. g. Cable Insulation):	crosslinked Silicone Rubber

Criteria for Selecting Suitable Crosslinking Peroxides

There are different criteria that have to be taken into account when it comes to choosing the right organic peroxide for the desired application:

- Crosslinking Performance of organic peroxides
- Safe Processing Temperature (Scorch Temperature), Crosslinking Temperature and Duration
- Physical Form and Properties of Crosslinking Peroxides / Peroxide Formulations and their Decomposition Products

Crosslinking Performance of Organic Peroxides

The crosslinking performance of an organic peroxide depends on the ability of its radicals to abstract hydrogen atoms from the polymer chain and therefore to induce a crosslinking reaction. The molecular structure of an organic peroxide is also responsible for its activity, i. e. the temperature at which it decomposes into radicals.

Table 5: Organic Peroxides suitable for Crosslinking Reaction in ascending activity

PEROXAN...	Scorch Temp. [°C] >20 min.	Formulation								Supply form			
		Techn. Pure	Silicone oil	Chalk	Kaolin	Silica	EPM	PE	EVA	Liquid	Paste	Powder	Granules
BD-Paste 50 SI	75		X								X		
BP-Paste 50 SI	85		X								X		
PB	100	X								X			
PB-50 P	100			X								X	
PK295 MB	115						X						X
PK295 P	115			X								X	
PK295 GS	115			X									X
BV-40 P	125			X								X	
BV-40 GS	125			X									X
DC	130	X											X
DC-P	130	X										X	
DC-P +	130	X										X	
DC-Paste 50 SI/3	130		X								X		
DC-40 PK	130				X							X	
DC-40 P	130			X								X	
DC-40 MB	130						X						X
DC-40 GS	130			X									X
DC-40 PE-G	130							X					X
DC-40 PE-MB	130							X					MB
BIB-1	135	X										X	
BIB-40 EV-G	135								X				X
BIB-40 GS	135			X									X
BIB-40 GS+	135			X									X
BIB-40 MB	135						X						X
BIB-40 P	135			X								X	
BIB-40 PK	135				X							X	
BIB-40 GS-K	135				X								X
BIB-40 PE-G	135							X					X
BU	135	X								X			
BU-50 P	135			X								X	
HX	135	X								X			
HX-Paste 75 SI	135		X								X		
HX-Paste 70 SH	135										X		
HX-50 PS	135					X						X	
HX-45 SP	135		SI Rubber								X		
HX-Paste 45 SI	135		X								X		
HX-45 GS	135			X									X
HX-45 MB	135						X						X
HX-26 TA	135			X TAIC								X	
HX-45 P	135			X								X	
DB	145	X								X			
HXY-85 W	145									W-ÖI	X		
HXY-45 P	145			X								X	

MB=Master batch

Safe Processing Temperature (Scorch Temperature), Crosslinking Temperature and Duration

Before the crosslinking reaction can be performed the raw materials (polymer(s)/elastomer(s), additives, Organic Peroxide) have to be homogenized by use of a mixing mill, an extruder or similar. Even if the temperature sensitive Organic Peroxide will be the last raw material which is added for homogenization to the compound, one has to avoid temperatures at which the peroxide decomposes and the crosslinking reaction starts during compounding.

After homogenization the compound has to be shaped to the final parts (e. g. yielding a radiator hose). This can be done by utilizing common processes for plastic processing, like casting, extrusion, pressing, sinter processes and calendaring. Due to the viscosity and melting range of the compound certain minimum temperatures are also required for these processes.

The maximum processing temperature of an Organic Peroxide is called the *safe processing temperature* or *scorch temperature*. Often this parameter is stated at the safe processing temperature t_2 , the temperature at which the scorch time is > 20 min.

Table 6: Scorch and Crosslinking Times of Organic Peroxides

Temperature [°C]	70	80	90	100	110	120	130	140	150	160	170	180	190	200
PEROXAN BD...														
Safe Processing Time [min]	47	12	2											
Crosslinking Time [min]			10	4	2									
PEROXAN BP...														
Safe Processing Time [min]		42	14	5										
Crosslinking Time [min]			72	22	7									
PEROXAN PB...														
Safe Processing Time [min]			29	20	11									
Crosslinking Time [min]						61	30	12	5					
PEROXAN PK 295...														
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

Crosslinking reactions are mainly performed in absence of ambient air, resp. in the presence of inert gases, as the Oxygen of the ambient air inhibits the radicals. The heat transfer to the polymer/elastomer to be crosslinked will be performed by utilizing either gases (e. g. steam, air or Nitrogen), melted salt bathes, heat radiation or microwaves. Depending on the apparative facilities only limited temperature ranges for the crosslinking reaction can be achieved. This has to be taken into consideration for the selection of a suitable peroxide.

The *crosslinking temperature* is either given as a function of the crosslinking duration or as t_{90} , the temperature at which 90% of all C-C links are performed within a time of 12 min.

The crosslinking duration for a given system consisting of polymer/elastomer and Organic Peroxide depends mainly on the rate of peroxide decomposition. The *half life time* (the time at a given temperature at which 50% of the Organic Peroxide has decomposed into radicals) is therefore a first indication for the required crosslinking duration. A total decomposition of any peroxide is achieved if the crosslinking duration is equivalent to 10 times the half life time at the chosen crosslinking temperature.

Besides a few exceptions the crosslinking duration can only be decreased by increasing the crosslinking temperature. An increase of 10° C will result in a 2 to 3 times higher decomposition rate of the peroxide. Accelerators, which are normally used to increase the rate of peroxide decomposition are ineffective or not practicable, as they will decrease strongly the storage life of the compound and/or influence the scorch temperature.

Physical Form and Properties of Crosslinking Peroxides / Peroxide Formulations and their Decomposition Products

The table 7 is listing the physical form and properties of crosslinking peroxides as well as their decomposition products.

Table 7: Physical Form and Properties of Crosslinking Peroxides / Peroxide Formulations and their Decomposition Products

<p>Physical Form: <u>Technical Pure Peroxides:</u> solids or liquids</p> <p><u>Peroxide Formulations:</u> liquids (OMS, Phthalates), pastes (Silicone Oil), solids (Chalk, Clay, Silica) masterbatches (EPDM, PE, EVA)</p>	<p><u>Liquid Formulations:</u> direct extruder injection, homogenization by migration</p> <p><u>Pastes:</u> Silicone Rubber only</p> <p><u>Solids (Powder and Granules):</u> common compounding methods (powders: compounding with low shear forces granules: dust free processing)</p> <p><u>Masterbatches:</u> no influence of fillers on final product properties</p>
<p>Safety Aspects: <u>Organic Peroxides are Class 5.2. Dangerous Materials</u></p> <p><u>Volatility / Boiling Point</u></p>	<p>Storage temperature: + 5° C to + 30° C</p> <p><u>Exception:</u> formulations of PEROXAN DC / PEROXAN BIB-1 with a peroxide content ≤ 40 %: no dangerous materials</p> <p>for certain peroxides crosslinking and/or compounding in closed systems is required</p>
<p>Decomposition Products:</p>	<p><u>Volatile and Odorless:</u> no influence on crosslinked parts</p> <p><u>Not Volatile, not Odorless:</u> restrictions in use of crosslinked parts</p> <p><u>Not Volatile, but Odorless:</u> no influence on crosslinked parts, but blooming may occur</p>
<p>Coagents and Additives:</p>	<p><u>Triallycyanurate/Triallylisocyanurate:</u> increases degree of crosslinking</p> <p><u>Phenolic Compounds:</u> may act as scorch retarder (increases scorch time)</p> <p><u>Other Additives:</u> may consume radicals and a higher Peroxide dosage is required</p>

Coagents, Influence of Additives in the Compound on Organic Peroxides

Substances like Triallylcyanurate or Triallylisocyanurate increase the degree of crosslinking. These materials act as multifunctional monomers and increase the number of links between the polymer chains. This reaction is similar to a graft polymerisation.

Phenolic compounds and others will inhibit the crosslinking reaction and can be utilized as scorch retarding agents. But at the same time they decrease the degree of crosslinking. To avoid this, a higher peroxide dosage is required.

Plasticizers, fillers, carbon black, colouring pigments, antioxidants, UV and Ozone protecting agents in the compound may consume radicals, e. g. by adsorption. This has to be matched by a higher dosage of the Organic Peroxide. In table 8 you can find a selection of dosage recommendations for various Polymers/Elastomers.

Table 8: Dosage Levels of Selected Common Peroxide Formulations for several Polymers/Elastomers

Polymer	Parts of Peroxide per 100 parts of Polymer/Elastomer				
	PEROXAN PK-295 P	PEROXAN BV-40 P	PEROXAN DC-40 P	PEROXAN BIB-40 P	PEROXAN HX-45 P
NR, IR	2,3 - 4,6	2,5 - 5,0	2,0 - 4,0	1,3 - 2,4	1,9 - 3,8
BR	1,0 - 2,0	1,1 - 2,3	0,9 - 2,0	0,5 - 1,1	0,8 - 1,8
CR	1,1 - 3,0	1,3 - 3,3	1,0 - 2,6	0,6 - 1,6	1,0 - 2,5
SBR	1,9 - 4,0	2,1 - 4,6	1,7 - 3,6	1,1 - 2,2	1,6 - 2,4
EPM, EPDM	6,9 - 11,0	7,5 - 12,5	6,0 - 10,0	3,8 - 6,2	5,8 - 9,5
PE	1,5 - 7,5	1,7 - 8,4	1,4 - 6,6	0,8 - 4,0	1,2 - 6,3
CM	6,8 - 10,5	7,5 - 11,7	6,1 - 9,4	3,8 - 5,8	5,7 - 9,1
EVA	2,6 - 5,2	2,9 - 5,8	2,4 - 4,5	1,5 - 3,0	2,2 - 4,4
t ₉₀ (crosslinking)	145 °C	160 °C	170 °C	175 °C	175 °C
t ₂ (safe process.)	115 °C	125 °C	130 °C	135 °C	135 °C

Satisfactory mechanical properties can already be obtained at the lower Peroxide dosage levels. Compression set properties improve with higher dosage levels. The upper dosage levels should not be surpassed, otherwise the remaining mechanical properties of the crosslinked parts will decrease. However, higher dosage levels are necessary if the compound contains radical consuming substances, as outlined in the last chapter.

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PERGAN
PERGAN Marshall LLC

PERGAN Marshall LLC
710 Bussey Rd Marshall, TX 75670 USA
Tel.: +1 903-938-5141

info@perganmarshall.com

PERGAN
The Peroxide Company

PERGAN GmbH
Schlavenhorst 71 46395 Bocholt Deutschland
Tel.: + 49 (0) 2871 / 99 02-0
Fax: + 49 (0) 2871 / 99 02-50

info@pergan.com

PERGAN
天津博金精细化工有限公司

Pergan Fine Chemical (TianJin) Co. Ltd.
Maotiao Road, Nanhe Industrial Zone, Xiqing District
Tianjin, 300382 P.R. CHINA
Tel.: + 86-22-23982200
Fax: + 86-22-23983300

yeekew@yahoo.com