QUALITY PERFORMS.

High-performance curing systems

Rhenogran® Perkalink® Vulcuren®

RheinChemie Additives

QUALITY WORKS.

LANXESS Energizing Chemistry

SULFUR DONORS
AND THEIR ADVANTAGES

Requirements for compounds and finished parts
The efficient production of technical rubber goods and tires requires high output, quality, and safety in all stages of processing.

Rhein Chemie aims to support customers in meeting current demands on health and safety, such as:
- Non-toxic, N-nitrosamine- and DPG-free curing systems
- Reduction of VOC and hazardous substances in production
- REACH regulation (for production and use)
- Environmental compatibility (international and European directives)

To achieve excellent quality, fulfill the increasing demands of the product life cycle and optimize processing and manufacturing, we offer versatile options for various curing systems and different rubbers. Our products are effective to optimize physical and dynamical performance of vulcanizates.

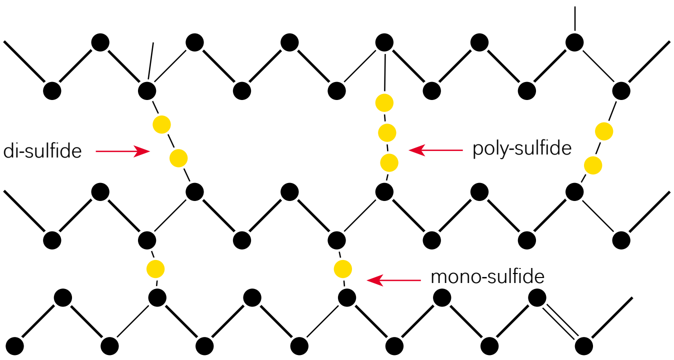
Rhein Chemie delivers superior quality products and services backed by decades of industry-wide experience in formulation mixing technologies, and technical expertise. And this pays for you.

Sulfur donors are of particular interest to the rubber industry, because they make it possible to fulfill special requirements. These organic compounds contain sulfur in a thermally labile form. Under normal curing conditions, free sulfur is released which, in contrast to normal sulfur, mainly forms mono- and di-sulfidic bridges. Because of their higher bond energies, these di-sulfidic bridges are much more resistant to reversion and are responsible for the excellent heat-aging resistance of the vulcanizates.

Replacing sulfur with sulfur donors results in less free sulfur in the rubber compound formulation, and this leads to advantages, such as:
- Improved physical properties
- Lower compression set
- Excellent reversion resistance
- Vulcanizates with improved aging resistance
- No sulfur blooming
- No contact staining with heavy metals
- Higher processing safety (scorch)

Increasing network strength/reversion resistance

Properties	Crosslinks	Bond energy [kJ/mol]
	C–C	346
Mono-sulfide	C–S–C	285
Di-sulfide	C–S–S–C	268
Poly-sulfide	C–Sx–C	< 268



Sulfur donor classification by reactivity

Sulfur donor

- 4,4'-dithiomorpholine (DTDM)*
- Alkylphenol sulfides
- **Caprolactam disulfide (CLD)**

Sulfur donor plus accelerator

- Dipentamethylene thiuram tetrasulfide (DPTT)*
- Tetramethylthiuram disulfide (TMTD)*
- Tetrabenzylthiuram disulfide (TBzTD)
- **Di-(2-ethyl)hexylphosphorylpolysulfide (SDT)**

* = N-nitrosamine-generating

Dosage

Nitrosamine-generating sulfur donors can be replaced by non-toxic caprolactam disulfide (CLD, sulfur donor) or dithiophosphates (e.g. SDT, sulfur donor plus accelerator) in all common sulfur-curable rubbers using standard, semi-EV (efficient vulcanization) and EV curing systems. All common primary and secondary accelerators, activators and retarders are compatible.

- **Standard sulfur system:** >1 phr sulfur/insoluble sulfur, usually without sulfur donor. Additionally 0.2–1.0 phr sulfur donor to improve the physical properties of the vulcanizates
- **Semi EV (efficient vulcanization) system:** 0.5–1.0 phr sulfur/insoluble sulfur and 1.0–3.0 phr sulfur donor
- **EV (efficient vulcanization) system:** no sulfur or 0.1–0.4 phr sulfur/insoluble sulfur and 3.0–6.0 phr sulfur donor (also as combinations, e.g. CLD, SDT, TBzTD or others)

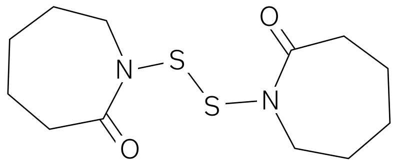
General dosage recommendation for NR, SBR, NBR, IIR, EPDM

	Product examples	Standard (phr)	Semi-EV (phr)	EV (phr)	Substance
Sulfur	Rhenogran® S-80, IS 90-65	1.0-3.0	0.5-1.0	0.0-0.4	Sulfur or insoluble sulfur
Sulfur donors	Rhenogran® CLD-80	0.2-1.0	1.0-3.0	3.0-6.0	Caprolactam disulfide (CLD)
	Rhenogran® SDT-50	0.2-1.0	1.0-3.0	3.0-6.0	Alkyl thiophosphorylsulfide (SDT)
Primary accelerators	Rhenogran® MBT-80, MBTS-70	0.5-2.0	0.5-2.0	0.5-2.0	Thiazoles
	Rhenogran® CBS-80, TBBS-80	0.5-2.0	0.5-2.0	0.5-2.0	Sulfenamides
Secondary accelerators	Rhenogran® TP-50, ZBOP-50, ZDT-50	0.5-4.0	0.5-4.0	0.5-4.0	Zinc alkyl thiophosphoryl (DTP)
	Rhenogran® ZBEC-70	0.3-1.0	0.3-1.0	0.3-1.0	Carbamate, zinc benzyl dithiocarbamate
Retarder	Rhenogran® Retarder E-80	0.2-0.8	0.2-0.8	0.2-0.8	N-phenyl-N-(trichlormethyl)thiobenzol sulfonamide
	Rhenogran® CTP-80	0.2-0.8	0.2-0.8	0.2-0.8	N-cyclohexylthiophthalimide (CTP)

SULFUR DONORS

Rhenogran® CLD-80 (caprolactam disulfide)

Rhenogran® CLD-80



Chemical structure of CLD

Dithiodicaprolactam

[N, N'-di-thio-bis(hexahydro-2H-azepinone-2)]

The sulfur donor CLD is an amide that does not form nitrosatable breakdown products. It therefore is a safe alternative for replacing morpholine disulfide (DTDM) as a sulfur donor with a comparable property profile. CLD is non-blooming and works in synergy with the primary accelerators in all common elastomers, such as NR, SBR, NBR, IIR and EPDM.

Rhenogran® CLD-80 can be used in rubber compounds when good temperature stability under dynamic-mechanical stress and, in general, physical properties providing long-term durability are required.

Rhenogran® CLD-80 is recommended if a retarding effect is needed followed by rapid vulcanization with improved reversion resistance, particularly for large molded parts or injection molding, where process safety is of the utmost importance.

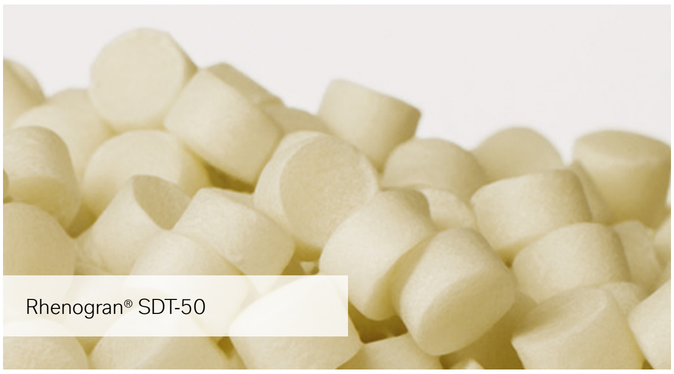
Advantages for curing properties

- Formation of mono- and di-sulfidic bridges
- Increased scorch safety
- Rapid vulcanization as soon as the curing temperature is reached (advantage for large molded articles)
- Wide curing plateau (advantage for high-temperature processing, e.g. salt bath vulcanization and injection molding)

Advantages for vulcanizates

- No reversion effect, heat-aging resistance of vulcanizates
- Good compression set, low permanent elongation
- Antioxidants often can be reduced
- Reduced blooming (compared to e.g. thiuram disulfides as crosslinking agents)

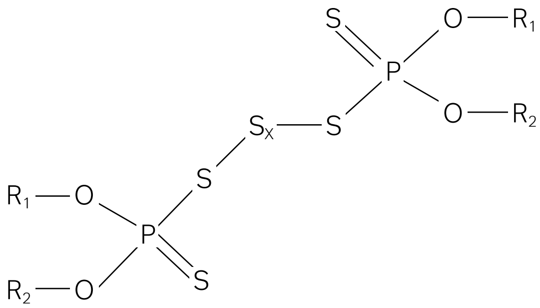
Rhenogran® SDT-50 (sulfur donor thiophosphate)



Rhenogran® SDT-50

SDT dithiophosphate is also available as Rhenocure® SDT/S (liquid carried on silica).

Rhenogran® SDT-50 as a secondary accelerator can replace nitrosamine-generating dithiocarbamates and thiurams in combination with thiazoles or sulfenamides. The accelerator and sulfur donor Rhenogran® SDT-50 combined with other additives results in the optimal compression set of vulcanizates and makes it possible to replace the OTOS accelerator in natural rubber, particularly in anti-vibration technology.



Basic chemical structure of dithiophosphates

Advantages for curing properties

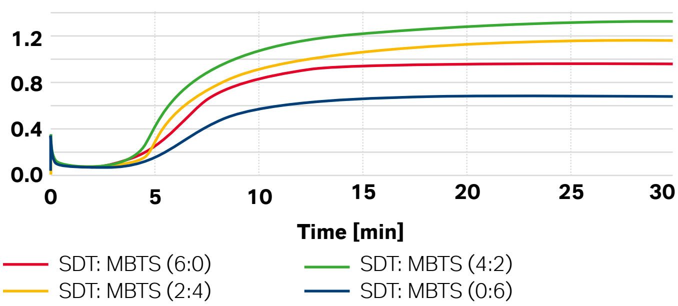
- Formation of mono- and di-sulfidic bridges
- Safe, nitrosamine-free curing
- No generation of odorous amines
- Easily dispersible, high loading possible
- No dispersion issues due to liquid form
- Rapid curing, accelerator speed widely adjustable (in combination with primary accelerators)
- Produces smooth extrudates

Advantages for vulcanizates

- Low compression set, good heat resistance
- Reduced blooming
- No reversion effects
  - Heat-aging resistance
  - Low heat build-up

Excellent solubility is an indicator of the good compatibility of dithiophosphates, especially SDT, with a wide range of polymers. As for all dithiophosphates, the accelerating and crosslinking effect of Rhenogran® SDT-50 is widely adjustable by varying the dosage.

Rheometer 150°C of SDT/MBTS compounds



Adjustment of acceleration with SDT/MBTS

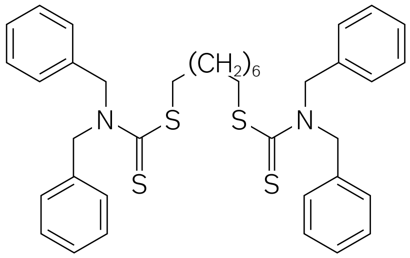
For SSBR/BR-based silica compounds with a high performance level for tire applications, the sulfur donors CLD and particularly SDT will improve reversion and outperform standard curatives in terms of the heat stability of the dynamic network. The dynamic properties indicate a positive impact on filler dispersion and silane coupling efficiency, as well good rolling resistance of the compounds. In addition, it is possible to eliminate or reduce the DPG (diphenyl guanidine) accelerator without sacrificing key physical properties. These curing agents therefore are the products of choice for modern rubber applications.

General dosage recommendation for NR, SBR, NBR, IIR, EPDM

		Rubber polarity →				
Chemicals (pure)	**mp (°C)**	**EPDM (phr)**	**NR (phr)**	**BR (phr)**	**SBR (phr)**	**NBR (phr)**
Sulfur	119	< 1.5	< 3.0	< 2.5	< 3.0	< 1.0
Insoluble sulfur	< 90	< 0.5	< 0.5	< 0.5	< 0.5	< 2.0
TMTD	137	< 0.5	< 0.5	n.a.	< 0.5	< 3.0
DTDM	130	< 1.5	< 2.5	n.a.	< 5.5	< 5.5
CLD	120	< 1.0	< 0.5	n.a.	< 1.0	< 0.5
TBBS	105	< 2.0	< 0.5	n.a.	< 0.5	< 5.0
MBT	179	< 1.0	< 2.0	< 2.5	< 1.5	< 1.0
MBTS	175	< 1.0	< 0.5	n.a.	< 0.5	< 1.0
ZDMC	250	< 0.5	< 0.5	< 0.5	< 0.5	< 1.5
ZDEC	175	< 0.5	< 0.5	< 0.5	< 0.05	< 3.5
TP	RT	< 6.0	< 1.5	< 6.0	< 6.0	< 7.0
SDT	**liquid**	**< 7.0**	**< 6.5**	**< 6.0**	**< 6.0**	**< 6.0**
ZBOP	liquid	< 6.0	< 3.5	< 6.0	< 6.0	< 7.0

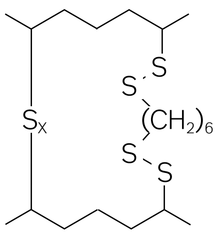
ANTI-REVERSION AGENTS AND CROSSLINKERS

Vulcuren®



Vulcuren®

Vulcuren® (1,6-bis(N,N'-dibenzylthiocarbamoyl-dithio)hexane) acts as a bifunctional crosslinker in the production of highly reversion-resistant vulcanizates. Flexible and thermodynamically stable hybrid crosslinks are formed during sulfur vulcanization in conventional or semi-efficient sulfur curing systems in combination with accelerators, such as mercaptobenzothiazoles or sulfonamides. Physically, sulfur-hydrocarbon-sulfur bridges are formed instead of regular sulfur-bridges.



In passenger tire treads based on SSBR/BR silica compounds, one major problem is the gradual hardening of the tread during its service life due to post-curing reactions and network alterations at high temperatures. Because the traction and wet grip of the tire are affected by hardening, this phenomenon should be avoided for safety reasons.

The heat stability of passenger tire tread compounds with Vulcuren® can be improved in comparison to compounds with a standard curing system. Vulcanization with Vulcuren® shows fast curing and a stable plateau. Physical as well as viscoelastic properties of the vulcanizates can be easily achieved. But the most significant advantage is the retention of dynamic behavior after aging (storage modulus, fatigue resistance).

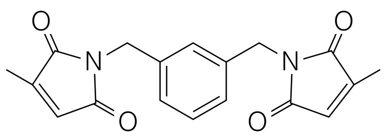
General dosage recommendation

Application (NR, BR, SBR)	Dosage (phr)
Anti-reversion agent	2.0 – 4.0
Crosslinker/secondary accelerator	0.3 – 1.0

Natural and synthetic rubber vulcanizates with Vulcuren® change only marginally during overcure due to the special crosslinking structure. High performance tread compounds with a Vulcuren® curing system can be expected to be advantageous wherever it is crucial to retain properties during their service life under severe conditions, such as high service temperatures.

Perkalink® 900

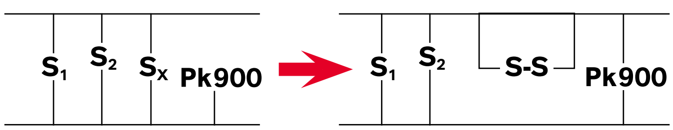
Reversion (thermal degradation) of sulfur crosslinks occurs either when sulfur-vulcanized rubber compounds are exposed to elevated curing temperatures for extended periods, or later during the service life of a rubber product, particularly when it is exposed to mechanical stresses under elevated temperature conditions.



Perkalink® 900

Perkalink® 900 protects sulfur-vulcanized rubber compounds from the unwanted effects of thermal degradation, such as reduced physical properties and decreased performance characteristics. Unlike with many other additives, the processing and cure properties (scorch delay, vulcanization rate and cure time) remain unaffected, because Perkalink® 900 is not reactive during vulcanization or at low temperatures.

When sulfur crosslinks degrade during curing or a product's service life, Perkalink® 900 compensates for the loss of sulfur bridges by reacting with the dienes/trienes in the polymer backbone and forming new, thermally stable carbon crosslinks that help to maintain physical and performance properties. The increased rate of reversion at higher temperatures is balanced out by increased reactivity.



Therefore, Perkalink® 900 is very effective in the presence of many unstable polysulfidic crosslinks, such as NR and IR rubbers, or polymer blends (> 50 % NR/IR with BR, SBR or other unsaturated polymers). Key applications are in thick cross-section components, where severe surface reversion may occur due to extended curing cycles. Consequently, higher curing temperatures can be applied to achieve improved productivity.

Perkalink® 900 is recommended for use in tire compounds, e.g. tread, carcass, NR steel, skim and retreading.

Truck tire test results (drum and road)

- 10 – 12 °C reduction in heat build-up
- 15 % improvement in endurance mileage
- 7 – 10 % reduction in rolling resistance
- Improved tread wear pattern

Perkalink® 900 also is the agent of choice for technical rubber articles when an anti-reversion agent is required. The beneficial effect of Perkalink® 900 on a rubber compound is clearly demonstrated by the improvement in heat build-up under harsh conditions.

Use in technical rubber articles

- Suspension bushings
- Engine mounts
- Fenders
- Conveyor belts

Because the number of compensating crosslinks is directly related to the concentration, the dosage level of Perkalink® 900 depends on the type of polymer and curing system used. After exposure to elevated temperatures, a higher overall crosslink density may influence the physical properties of the vulcanizates, particularly at increased dosage levels, meaning that it is of mandatory importance to adjust the Perkalink® 900 concentration.

General dosage recommendation

Polymer system	Cure system	Perkalink® 900 concentration (phr)
100% NR, IR or blend with > 50% NR, IR	EV to SEV SEV to conventional high sulfur	0.25 - 0.40 0.50 - 0.75 0.50 - 0.75
SBR/BR blends	SEV to conventional	0.25 - 0.40
Other unsaturated polymers e.g.NBR	SEV to conventional	0.25 - 0.50

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