EVONIK INDUSTRIES

VESTENAMER®

Rubber additive
with unique properties

VESTENAMER®

Evonik. Power to create.

Evonik, the creative industrial group from Germany, is one of the world leaders in specialty chemicals. Its activities focus on the key megatrends health, nutrition, resource efficiency and globalization. Evonik is active in over 100 countries around the world.

The High Performance Polymers Business Line produces customized products, systems, and semi-finished products based on high performance polymers. Our plastics have proven their worth in various applications for more than 50 years.

VESTENAMER® was developed at the beginning of the 1970s as a processing aid for the tire industry. It is one of the first polymers to be commercially produced in a ring-opening metathesis polymerization.

Evonik. Power to create.

Content

VESTENAMER®

VESTENAMER® is a semicrystalline rubber that is also described as a polytransoctenamer rubber (TOR). As a polymeric processing aid, it acts as a plasticizer of rubber compounds in mixing and manufacturing processes. In the vulcanization of rubber parts, it participates in crosslinking and, as an elastomer, is fully incorporated into the network.

The properties of VESTENAMER®:

- **Low melting point (<60 °C)**
- **low viscosity in the melt (Mooney <10)**
- **high cristallinity**
- **high percentage of macrocycles (>30 %)**
- **a double bond every eighth carbon atom**

Low viscosity above the melting point

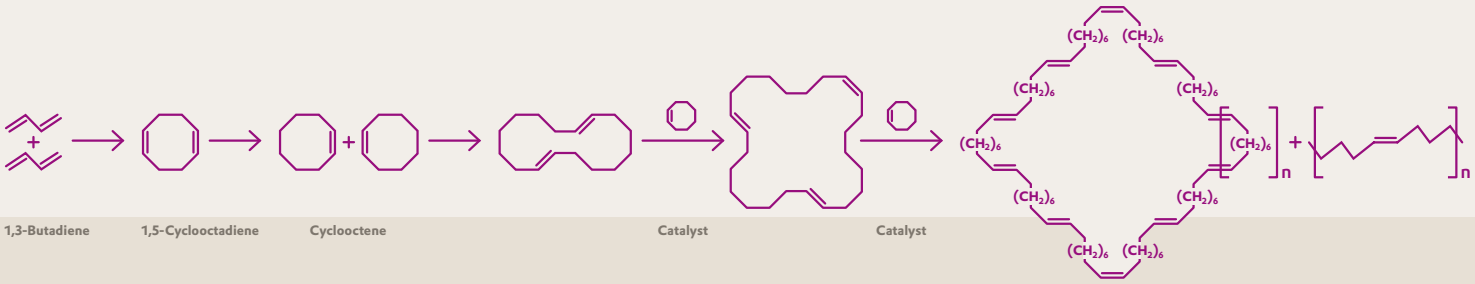
VESTENAMER® semicrystalline rubber has a high macrocycle content that significantly reduces its molecular weight. Unlike linear macromolecules, macrocycles can crosslink to a completely three-dimensional network, even at low molecular weight. Combined with a broad molecular weight distribution, its low molecular weight is also responsible for its unusually low viscosity at higher temperatures. Above its melting temperature at 100 °C (T_m <60 °C), VESTENAMER® is a low-viscosity melt with Mooney values lower than 10.

Double bond content

On metathesis polymerization, the double bond of the monomer cyclooctene is preserved so that the resulting transpolyoctenamer contains a double bond at every eighth carbon atom. This is why the vulcanization speed is somewhat lower than for SBR. VESTENAMER® vulcanizes with all crosslinking agents commonly used in rubber curing, such as sulfur, sulfur donors, peroxides and curing resins.

Chemistry

VESTENAMER® is produced in a ring-opening metathesis polymerization (ROMP) starting from 1,5-cyclooctadiene to cyclooctene as an intermediate. The polyoctenamer consists of linear and cyclic macromolecules. The *cis/trans* ratio, which determines the degree of crystallinity of TOR, is controlled by the polymerization conditions. In general, if trans content is increased, a higher crystallinity is produced and thus a higher melting point can be obtained. The crystallinity is thermally reversible, and the crystallization rate is exceptionally high. This effect can be used to reduce the cold flow of soft compounds, for example, to improve green strength and reduce shrinkage in calendering.



Reactive additive

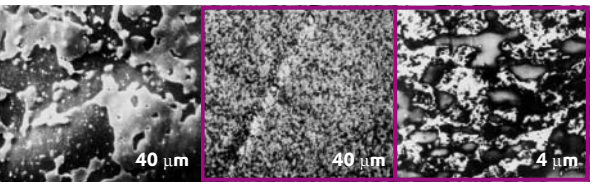
The trans-double-bond content of VESTENAMER® is nearly 80%, which results in high crystallinity of about 30%. The melting point is 54 °C, and the melt displays a honey-like consistency, the granules are light opaque. VESTENAMER® is stabilized with sterically hindered phenolic antioxidants.

Characteristic values of VESTENAMER® 8012

Property	Method	Unit	Value
Molecular weight, Mw	GPC	–	90,000
Glas transition temperature, Tg	ISO 6721	°C	-65
Crystallinity at 23 °C	DSC (2nd heating)	%	~30
Melting point	DSC (2nd heating)	°C	54
Thermal degradation	TGA	°C	275
Cis/trans ratio of double bonds	IR	%	20:80
Mooney viscosity ML (1+4) 100 °C	DIN 53 523	–	<10
Viscosity number J/23 °C	ISO 1628-1	ml/g	120
Ash content	DIN 53 568, part 1	%	max 0.1
Volatile substances (1h/105 °C)	DIN 53 526 ISO 248	%	max 0.5
Density	DIN 53 479 A	g/cm³	0.91
Melt viscosity MVR 190/2.16	ISO 1133	m³/10 min	18
Melt viscosity MVR 190/5	ISO 1133	m³/10 min	50
Melt viscosity MVR 230/2.16	ISO 1133	m³/10 min	28
Melt viscosity MVR 230/5	ISO 1133	m³/10 min	78
Stress at yield	ISO 527	MPa	7.5
Strain at yield	ISO 527	%	25
Stress at break	ISO 527	MPa	8.5
Strain at break	ISO 527	%	400
CHARPY impact strength -20 °C	ISO 179/1eU	kJ/m²	N
Tensile strength 23°C	ISO 8256	kJ/m²	164
Tensile strength 0 °C	ISO 8256	kJ/m²	190
Tensile strength -20 °C	ISO 8256	kJ/m²	240
IZOD notched impact strength 23 °C	ISO 180/1 A	kJ/m²	N
IZOD notched impact strength 0 °C	ISO 180/1 A	kJ/m²	22
IZOD notched impact strength -20 °C	ISO 180/1 A	kJ/m²	19

N = no break

VESTENAMER®
in rubber compounds



VESTENAMER® significantly increases the compatibility of NBR and EPDM rubber.

From left to right:
EPDM/NBR 50:50
EPDM/NBR/VESTENAMER® 40:40:20
in the resolution 40 µm and 4 µm

Improving the dispersion of additives

The homogeneity of rubber compounds—the distribution of fillers and additives—is improved by adding small amounts of VESTENAMER®. Initially, this causes no appreciable reduction in viscosity but rather a slight increase in some cases. When adding higher amounts of VESTENAMER® however, the viscosity lowering effect predominates.

The opportunity to reduce the mixing viscosity and therefore increase the flowability of the compound by exchanging some of the basic polymers for TOR plays an important role in making difficult compounds—those with low or no plasticizer content—controllable and improving fabric penetration.

Improving compatibility

VESTENAMER® enables the mixing of otherwise incompatible polymers. Some of these include

- Polar and nonpolar rubbers (e.g. EPDM and NBR)
- Emulsion and solution rubbers
- Polyolefin compounds

Influence on the vulcanizate

The content of VESTENAMER® determines the physical properties of the compounds. In general, hardness and modulus are increased, whereas tensile strength, strain at break and tear resistance are slightly decreased. For the most parts, the dynamic properties are also improved, as demonstrated by the reduced heat buildup in fatigue tests.

Improved processability of natural rubbers

It is well known that the degree of polymer degradation or "mastication" has a decisive impact on the processability of natural rubber (NR). In the presence of VESTENAMER®, this degradation is reduced and even prevented at higher concentrations. At the same time, the viscosity level of the NR/VESTENAMER® blend is reduced significantly.
This behavior opens an opportunity to selectively tune the viscosity of the natural rubber compound through plasticization with VESTENAMER® and, at the same time, reduce mastication.

- In multi-stage treatment processes, such as the reprocessing of reject batches, the drop in viscosity compared to the pure natural rubber compound decreases as the quantity of TOR is increased.
- Rheometer data shows that the vulcanization speed of the blends with increased TOR content is somewhat slower. This effect is reduced, however, the higher the vulcanization temperature is.
- Tests prove that VESTENAMER® significantly improves the reversion stability of natural rubber, especially at higher vulcanization temperatures.
- Depending on the past history of the compound with regard to mastication, compounding and further processing, the reduced degradation and decreased reversion can increase key vulcanizate values. Examples of these attractive improvements in properties are modulus increase, improved compression set, reduced heat development with dynamic loading. The effects are stronger the higher the shear load during the entire treatment process, and the higher the vulcanization temperature and the longer the vulcanization time.
- VESTENAMER® significantly improves the abrasion resistance of natural rubber compounds.

Tires

Versatile applications

VESTENAMER® is used as a processing aid for the rubber industry, in the production of masterbatches, to increase the compatibility of rubber blends, and to simplify rubber recycling.

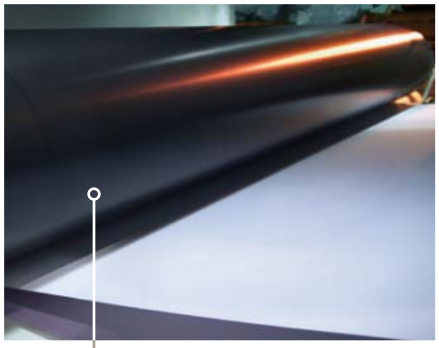
VESTENAMER® in tire production

Tire production was the first application field of VESTENAMER® and is still the most important. Adding only a small amount of VESTENAMER® pellets eases the mixing and processing of various tire compounds significantly.

VESTENAMER® also improves the dispersion of difficult polymer blends as it reduces the viscosity of the compound. At the same time, it has no effect on the dynamic properties of the vulcanizate. Especially modern tires (e.g. the "green tires") are highly filled and demanding in respect to additive dispersion and processing of the uncured rubber compound . VESTENAMER® improves the dispersion of additives significantly. In addition it contributes to the enhanced processibility.

The abrasion resistance or aging properties undergo little to no change when using VESTENAMER® and can even be improved. In addition, the reversion of NR rubbers at high vulcanization temperatures is reduced. Examples of applications are rim strips, beads and bead cores, and tread areas.

Profiles



Roller covers

Hoses

VESTENAMER® for technical rubber goods

Profile extrusion

In many areas, profile production benefits clearly from adding VESTENAMER®:

- Increase the stability of the raw profile
- Improve flowability
- Improve surface smoothness
- Increase dimensional stability

Use in extremely hard profiles (e.g. profile mounts for angle profiles) is a particularly time-tested application. Here, VESTENAMER® results not only in increased vulcanization strength but significantly improved processability.

Roller covers

Because of its high crystallinity and high macrocycle content, which enhances dimensional stability, the use of VESTENAMER® minimizes shrinkage and reduces anisotropy of calendered products.

VESTENAMER® also ensures an improved surface finish, because it migrates to the surface during the hardening process.

Because it acts as a softener in the uncured compound, VESTENAMER® also improves fabric penetration. The increased green strength makes roll covering easier, which means form is retained in the uncured state. Not least, the good flowability improves layer welding and prevents flow marks.

Cable extrusion

In cable extrusion, as in hose extrusion, VESTENAMER® reduces mixing energy in the inner mixer during compounding. Because of the lower output temperature of the compound in cable extrusion, mixing steps are reduced. VESTENAMER® also significantly improves the extrudate surface without impairing the physical and electrical properties of the vulcanizate. The double-bond content of the polyoctenamer may result in a marginal increase in the compression-set values, which can point to a lower polymerization density. VESTENAMER® is compatible with all rubber types with saturated or unsaturated hydrocarbon chains.

Hose production

Because compounds that contain VESTENAMER® have significantly reduced viscosity and improved flowability, the production of hoses such as brake hoses is simplified. Improved flowability at increased temperatures results in improved layer adhesion and increased penetration of the fabric used for reinforcement. Because of its crystallinity, VESTENAMER® results in a noticeable increase in hardness and green strength of the unvulcanized inner hoses already at ambient temperature — an effect that continues during cooling. In many cases, therefore, the use of an energy-intensive cooling process at subzero temperatures to increase hardness and green strength for the sake of decoupling can be limited or dispensed with entirely.

VESTENAMER® simplifies rubber recycling

Rubber waste becomes mats and road surfaces

An application that has proved its worth over many years is the addition of VESTENAMER® in the recycling of waste rubber for use in railroad crossings, floor coverings, mats and traffic guidance systems. Grinding waste rubber partially destroys its connective sulfur bridges. If adhesive is used to process the recycled rubber into new products, the parts will have poor surface quality, inadequate physical properties, and are very likely to fracture at contact points.

In contrast, VESTENAMER® rebuilds a macrocyclic network between sulfur and the ground rubber and thus improves physical properties and surface finish, and reduces the rejection rate, VESTENAMER®, therefore, improves both the cost-effectiveness of the rubber recycling process as well as the quality of the parts produced.

Asphalt

The use of VESTENAMER® in road construction came about from the experience of using it in rubber recycling: It involves mixing low quantities of VESTENAMER® with rubber powder from old tires (GTR) and adding it to bitumen or asphalt for road construction.

In contrast to non-reactive rubber powder, VESTENAMER® reacts to form a bituminous binder, resulting in a homogenous, hardly sticky, rubber-like composite, which can be applied to the road surface more easily. The VESTENAMER®/GTR compound gives roads improved resistance upon frequent heavy-load traffic. It can also contribute to reducing ice formation, noise emission, brittle-ness, and the formation of cracks. It also means that thinner layers often suffice in preventative maintenance measures.

VESTENAMER® granules in rubber powder

The use of VESTENAMER® improves the properties of the bitumen mixture and the processability of the asphaltes.

VESTENAMER® enhances the physical properties and the surface finish of recycling products.

Further application fields

Masterbatches

VESTENAMER®-bound batches are a beneficial alternative for preventing agglomeration when storing components for rubber compounds. The batches can be either granulated, cut into strips, or pressed through the mill. They are dust-free, can be stored in silos and conveyed automatically. This way, pre-dispersed additives meet all the requirements for safe rubber chemicals.

Solid-bound chemicals

In combination with mineral fillers, VESTENAMER® can be used as a polymer substrate for liquid chemicals to reduce problems of dosing.

Physiological and toxicological evaluation

Environmental compatibility and safety

VESTENAMER® is a water insoluble solid polymer that is not expected to have any adverse effects on plants, animals or microorganisms under environmental conditions. It is non-toxic, not subject to a labelling requirement within the meaning of the German Hazardous Substances Ordinance, and not hazardous for water. In conformity with the regulations of the local authorities, this polymer may be disposed of through dumping or burning, similar to household waste. Our Customer Service Center will supply you with an EC safety data sheet containing further information on request.

If VESTENAMER® is properly processed, no hazardous by-products are generated, though adequate ventilation and extraction of polluted air from the working areas should be ensured nonetheless.

Combustibility

With melt temperatures of higher than 250 °C – 300 °C, flammable gases are emitted during processing. Combustion with an adequate air supply yields carbon monoxide, carbon dioxide, and water. As the spectrum of cracking and combustion products depends to a large extent on the actual fire conditions, no general statements can be made here.

Food contact

Following the harmonization of European laws and ordinances, new regulations have come into effect for food contact plastics. Commission Regulation (EU) No. 10/2011 has applied since May 1, 2011. VESTENAMER® 8012 is approved for use in food contact polymers for which the food simulant A (ethanol 10 vol%) is defined, because its base monomer and additives are on the positive list in Commission Regulation (EU) No. 10/2011. A migration limit of 0.05 mg/kg cyclooctene, as well as migration limits for the additives, must be complied with on the finished article.

VESTENAMER® 8012 has not been approved by the FDA yet.

Toxicological properties

VESTENAMER® has an LD50 value of >12.500 mg/kg in rats (oral). The polyoctenamer causes no skin or eye irritation. In rats, oral intake of up to 4,000 mg/kg body weight over 90 days showed no toxic effects. Likewise, no mutagenic changes occurred with VESTENAMER® in the Ames test on Salmonella typhimurium (in vitro) and in the micronucleus test on mice.

For more detailed information and special inquiries, please contact us.

Handling and quality

As a rule, VESTENAMER® is supplied as cylindrical or lenticular pellets. It is delivered in polyethylene bags with a net weight of 25 kg each. One disposable pallet consists of 50 bags. Following production, the product is suitable for storage for a minimum of five years at temperatures of up to 30 °C and protected against direct sunlight.

Our proven quality management system, from development, through production, to quality assurance, ensures a high level of quality for VESTENAMER®. We are continually optimizing our ISO 9001:2008 quality management system, which has been certified since 1992. The positive resonance among our customers is palpable. Nearly all rated our services and the management system in the highest category.

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