Application of dithiophosphates to improve dynamic properties in silica compounds

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Abstract

Dithiophosphates show numerous improvements when used in silica filled compounds, e.g. for tire treads (Technical Report No. 68). Some of the challenges when using these co-accelerators in silica compounds are fast cure and viscosity increase over shelf life. New synergistic combinations with a tailor-made new processing stabilizer Rhenofit® GE 1914* help to overcome difficult mixing. Rhenocure® SDT/S and Rhenocure® ZBOP/S can substitute DPG in tire tread compounds. Very positive effects have been found with regard to heat stability, dynamic heat build-up as well as dynamic modulus and tan δ of the compound.

A solution SBR BR compound composed with a high load of silica, coupled with a disulfane type silane was mixed in three steps to achieve sufficient coupling. The formulation for testing is given in table 1. Mixing took place in a two-step internal mixing process and a final pass on the open mill.

*) Rhenofit® GE 1914 is the silica-bound form of GE1872. The active ingredient is 75%.
The rheometer chart shows that the exchange of DPG by either dithiophosphate leads to an increase in cross-linking density, evident by a higher torque. The further addition of the silica-specific processing promoter, Rhenofit® GE 1914, leads to a reduction of initial torque due to a lower viscosity and a higher curing rate (shorter t50, t90). The final torque however, remains high.

1. Higher cross-linking density and faster curing

The rheometer chart shows that the exchange of DPG by either dithiophosphate leads to an increase in cross-linking density, evident by a higher torque. The further addition of the silica-specific processing promoter, Rhenofit® GE 1914, leads to a reduction of initial torque due to a lower viscosity and a higher curing rate (shorter t50, t90). The final torque however, remains high.

Higher cross-link density with either single component dithiophosphates or in combination with the new processing stabilizer Rhenofit® GE 1914.
2. Excellent storage stability and shelf life

Measuring Mooney viscosity initially after mixing results in similar viscosity values for the control system and the dithiophosphate accelerated systems. After 7 days and 21 days of shelf life, however, dithiophosphate systems tend to increase by 10-20 Mooney units. To maintain excellent processability and low viscosities over three weeks below the level of the initial value of the control compound the addition of Rhenofit® GE 1914 at the recommended level of 2-3 phr is highly effective.

Fig. 2: Mooney viscosity before and after storage

Mooney viscosity shows no significant increase over shelf life when used in combination with Rhenofit® GE 1914.

3. Stable modulus and hardness at high temperatures

Hardness turns out 2-3 ShA units higher than the control system if DPG is replaced by dithiophosphates at a phr-equivalent level. When measuring ShA hardness at higher temperatures (100°C), dithiophosphate-cured compounds show almost no change in hardness while DPG cured compounds tend to soften, indicated by a reduction in hardness of about 12 ShA units. This means, hardness remains very stable between 23-100°C with advantages for the temperature independence of a compound under dynamic load (heat build-up). After aging 7 days at 100°C the compounds were hardening about the same degree as the control system. This behavior correlates with modulus 100 and 200 data.
Stable Shore A hardness over a wide temperature range (23-100°C) when dithiophosphates are used. The new process stabilizer Rhenofit® GE 1914 further improves aging properties of the compound.

4. High tensile strength and improved heat stability

The tensile strength and modulus 100 of dithiophosphate-accelerated systems is slightly higher than those of the control system. As a result, elongation at break is slightly reduced. After aging 7 days at 100°C particularly SDT-cured compounds show widely unchanged tensile strength due to the sulfur donor capacity of SDT. The process stabilizer Rhenofit® GE 1914 further improves aging properties of the compound.

Tensile strength is particularly stable when using Rhenocure® SDT/S or applying the process stabilizer Rhenofit® GE 1914.
5. Dynamic heat build-up

Compared to the control compound, dithiophosphate-cured samples showed considerably less heat build-up, reduced dynamic creep and a lower permanent set than the control system cured with DPG.

Fig. 5: Dynamic heat build-up in the Goodrich flexometer (70°C, 1 MPa)

Heat build-up significantly reduced: dithiophosphates can improve dynamic properties of silica compounds.

6. Dynamic mechanical testing

A look at the dynamic mechanical data (tan δ) shows a crossover of the tan δ curves of DPG systems with dithiophosphate systems in the temperature range around 0°C. Below this temperature the dithiophosphate systems provide better dampening of the compound thereby supporting wet grip and driving on snow or ice. Above that temperature dithiophosphate systems show a lower tan δ, hence contributing to a potentially improved rolling resistance.

Fig. 6: Loss tangent (tan δ) at lower temperatures (10 Hz, 2% strain)

Dithiophosphates support improved wet skid, better traction and breaking on snow or ice.
Specifically interesting is the crossover of the control system with the dithiophosphate systems in the temperature range of 0°C. With this specific property, dithiophosphates can offer advantages in the high temperature regime as well as in the low temperature regime of the dynamic modulus.

7. Conclusions

Dithiophosphates can be utilized as potential alternatives to classic co-accelerators in silica compound cross-linking. They provide high cross-linking density. Their shelf life and viscosity is easily controlled by the use of specific process stabilizers like Rhenofit® GE 1914. They show superior aging resistance and excellent high temperature stability of the vulcanizates. Moreover, they offer lower heat build-up and show advantages in dynamic behavior.

Potential advantages for the use of Rhenocure® SDT/S, Rhenocure® ZBOP/S also in combination with Rhenofit® GE 1914 in tire compounds are:

- Improved processing
- Shelf life stability
- Fast curing
- High temperature performance
- Improved aging resistance
- Reduced rolling resistance
- Improvements in wet skid and on ice
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