TECHNICAL UPDATE

CRAY VALLEY
Hydrocarbon Specialty Chemicals

Dymalink® 709 Enables Zinc Reduction in Accelerated Sulfur Vulcanization Through More Efficient Activation

Benefits

- Efficient activator for accelerated sulfur vulcanization
- Maintains cured physical properties at reduced loading of zinc salt
- Drastically reduces the molar concentration of zinc in the compound

Additional Information

MSDS/TDS: Dymalink® 709

Description

Dymalink® 709 demonstrates utility as a functional additive in compounds cured via sulfur vulcanization. The zinc salt of methacrylic acid can be used in place of traditional zinc oxide/stearic acid activating systems. Part for part, Dymalink 709 acts as a more efficient activator by increasing the number of crosslinks, while lowering the average sulfur rank of each linkage. As a corollary, Dymalink 709 can be used in place of zinc oxide (ZnO) to maintain optimal physical properties at significantly reduced concentrations of zinc in the compound. The potential for zinc reduction is demonstrated to be 1/2 to 1/5 the molar levels of traditional zinc-containing activators.

Features and typical properties of Dymalink 709 are presented below.

Dymalink® 709 Features and Typical Properties

Product Description	Zinc monomethacrylate
Product Features	• Monobasic metallic monomer • Potent activator for accelerated sulfur-cure
Physical Form	White powder
Molecular Weight	167
Specific Gravity @ 25 °C	1.88

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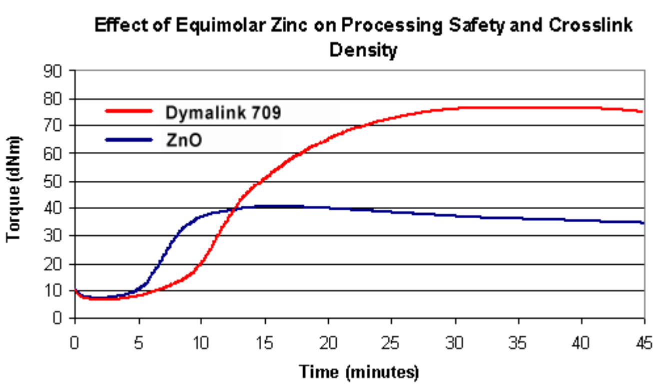
Previous work has demonstrated the potential to improve physical properties such as modulus and reversion resistance through equimolar replacement of ZnO with Dymalink 709. Prior results are provided in the figures below. As shown, equimolar replacement in a model cis-PI formulation resulted in significantly higher delta torque, 100% and 300% moduli, and Shore A hardness. Analysis verifies that through the use of Dymalink 709 more crosslinks of lower sulfur rank are formed. The data was acquired according to ASTM D5829, ASTM D412, ASTM D624(C), and ASTM D2240.

Model Formulation & Performance

Component / Property	ZnO-Based, phr	Dymalink® 709-Based, phr
Cis PI	100.0	100.0
Carbon black	50.0	50.0
Process oil	10.0	10.0
Antioxidant	1.0	1.0
Stearic acid	2.0	2.0
ZnO	**5.0**	**--**
Dymalink 709	**--**	**10.0**
Sulfur	2.5	2.5
TBBS	0.7	0.7
t_2, mins.	4.55	3.68
t_{90}, mins.	10.11	23.94
ML, dNm	8.4	6.2
MH, dNm	45.7	79.3
MH-ML, dNm	37.3	73.2
Shore A	55	62
Tensile strength, MPa	24.9	21.7
Elongation @ break, %	628	608
Modulus, 100%, MPa	2.0	2.7
Modulus, 300%, MPa	8.9	11.4
Die C tear, kN/m	58.4	51.3
Moles Zn/100 gms. Polymer	**0.063**	**0.063**



More recently, environmental concerns regarding the ultimate fate of unbound zinc species in rubber articles has led to increasing pressure on manufacturers to reduce the amount of ZnO or other zinc compounds in formulations. The increased activity of Dymalink 709 allows for a large reduction in the zinc concentration used to achieve similar ultimate physical properties. Reductions are achieved through a combination of increased efficiency of cure (lower phr zinc salt required) and a higher additive molecular weight. For example, even at equivalent phr loadings, Dymalink 709 contains roughly 1/2 the amount of zinc as ZnO.

Results from model formulations are provided below, including a tire sidewall, high performance silica tread, wirecoat compound, and model rubber roll. In each of these studies, the level of Dymalink 709 was optimized such that the rheometer profile and optimally cured physical properties were similar to the ZnO control. The resulting reduction in molar zinc concentration is highlighted.

Sidewall Formulation & Performance

Component / Property	ZnO-Based, phr	Dymalink® 709-Based, phr
Cis BR	50.0	50.0
NR	50.0	50.0
Carbon black	50.0	50.0
DAE oil	12.0	12.0
IPPD	2.0	2.0
TMQ	1.0	1.0
Stearic acid	0.8	0.8
ZnO	**5.0**	**--**
Dymalink 709	**--**	**2.0**
Sulfur	2.5	2.5
TBBS	0.7	0.7
t_2, mins.	3.62	3.21
t_{90}, mins.	6.31	5.85
ML, dNm	4.1	3.4
MH, dNm	30.9	30.3
MH-ML, dNm	26.9	26.8
Shore A	51	56
Tensile strength, MPa	22.8	23.2
Elongation @ break, %	738	758
Modulus, 100%, MPa	1.7	1.7
Modulus, 300%, MPa	6.5	6.5
Die C tear, kN/m	86.1	84.6
Moles Zn/100 gms. Polymer	**0.063**	**0.012**

Silica Tread Formulation & Performance

Component / Property	ZnO-Based, phr	Dymalink® 709-Based, phr
Cis BR	25.0	25.0
HVSSBR	75.0	75.0
Silica	65.0	65.0
Silane (50%)	10.4	10.4
DAE oil	25.0	25.0
IPPD	2.0	2.0
Stearic acid	1.0	1.0
ZnO	**5.0**	**--**
Dymalink 709	**--**	**2.5**
Sulfur	1.4	1.4
CBS	1.7	1.7
DPG	2.0	2.0
t_2, mins.	2.11	2.84
t_{90}, mins.	10.4	6.6
ML, dNm	5.6	5.8
MH, dNm	32.9	33.8
MH-ML, dNm	27.4	28.1
Shore A	53	52
Tensile strength, MPa	18.2	17.5
Elongation @ break, %	450	385
Modulus, 100%, MPa	2.1	2.6
Modulus, 300%, MPa	10.1	12.4
Die C tear, kN/m	43.9	38.0
Moles Zn/100 gms. Polymer	**0.063**	**0.015**

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Wirecoat Formulation & Performance

Component / Property	ZnO-Based, phr	Dymalink® 709-Based, phr
NR	100.0	100.0
Carbon black	65.0	65.0
DAE oil	3.0	3.0
TMQ	1.0	1.0
Stearic acid	2.0	2.0
ZnO	**5.0**	**--**
Dymalink 709	**--**	**5.0**
Sulfur	3.5	3.5
CBS	0.8	0.8
IPPD	1.0	1.0
t_2, mins.	0.86	1.05
t_{90}, mins.	3.06	5.36
ML, dNm	6.3	4.9
MH, dNm	50.7	56.4
MH-ML, dNm	44.5	51.5
Shore A	66	69
Tensile strength, MPa	26.4	25.1
Elongation @ break, %	518	481
Modulus, 100%, MPa	4.4	4.6
Modulus, 300%, MPa	16.0	16.5
Die C tear, kN/m	133.0	157.0
Moles Zn/100 gms. Polymer	**0.063**	**0.030**

Rubber Roll Formulation & Performance

Component / Property	ZnO-Based, phr	Dymalink® 709-Based, phr
NBR	100.0	100.0
Carbon black	50.0	50.0
DAE oil	10.0	10.0
IPPD	2.0	2.0
Stearic acid	0.8	0.8
ZnO	**5.0**	**--**
Dymalink 709	**--**	**2.0**
Sulfur	1.0	1.0
CBS	1.2	1.2
t_2, mins.	2.75	3.68
t_{90}, mins.	4.92	6.46
ML, dNm	3.5	3.3
MH, dNm	22.5	21.3
MH-ML, dNm	19.0	18.0
Shore A	62	64
Tensile strength, MPa	19.7	18.8
Elongation @ break, %	957	1005
Modulus, 100%, MPa	1.6	1.6
Modulus, 300%, MPa	5.1	4.6
Die C tear, kN/m	64.1	62.8
Moles Zn/100 gms. Polymer	**0.063**	**0.012**

Concluding Remarks

It is notable that application of the demonstrated technology will provide the most benefit in conventional and semi-efficient sulfur vulcanization systems. Available sulfur is a prerequisite to formation of the active sulfurating agent. It has been proposed that zinc sourced from the activator plays a central role in this reaction intermediate. It has also been proven that zinc monomethacrylate does not contribute to additional non-sulfur crosslinks when applied. Dymalink 709 should be considered in any zinc rationalization study, as the potential for significant reductions in zinc concentration exists.

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