

Maintenance of Mechanical and Viscoelastic Properties in Truck and Off-the-Road Tire Tread Compounds by Using 1,3 Bis(Citraconimidomethyl)benzene

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ABSTRACT: The effect of the antireversion agent 1,3 bis(citraconimidomethyl)benzene has been studied in a truck compound and a silica containing off-the-road compound. Laboratory results show that the antireversion agent significantly improves compound reversion resistance by means of a crosslink compensation mechanism. This improved reversion resistance provides a stabilization of viscoelastic properties on overcure and aging, which in turn should improve the performance of heavy duty tires with

regard to rolling resistance and heat buildup throughout their service life. The antireversion agent is particularly effective in stabilizing viscoelastic properties in combination with a reduced level of the saline coupling agent, TESPT. This offers improved tire performance at no cost penalty. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3689–3694, 2002

Key words: elastomers; additives; viscoelastic properties; crosslinking

INTRODUCTION

Large truck and off-the-road tires are frequently required to operate at high loads and high speeds for extended periods of time. These severe operating conditions result in greater heat buildup than would normally be encountered under less demanding service conditions. As a consequence, the excessive running temperatures lead to reversion in compound components, which may, in turn, lead to reduced tire durability or, in extreme circumstances, to tire failure.

Much effort has been expended over the years to improve the dynamic properties of tread compounds such that tire running temperatures and rolling resistance can be reduced and stabilized throughout the lifetime of the tire. An established approach is the use of so-called semiefficient cure systems comprising reduced sulphur levels and increased accelerator levels. However, although effective in improving viscoelastic properties, this approach is only partially successful because lowering of sulphur levels negatively influences other desirable properties such as tear and flex/fatigue life.

This article reports laboratory results concerning modifications to truck and off-the-road (OTR) tread compounds, with special reference to the antireversion agent 1,3 bis(citraconimidomethyl)benzene (Perkalink 900),^{1–9}

aimed at maintaining dynamic mechanical properties following overcure or aging.

EXPERIMENTAL

Compound formulations are listed in Tables I and II. Compounds were mixed according to procedures described in an earlier publication.¹

Cure characteristics were determined using an MDR 2000EA rheometer. Test specimens were vulcanized by compression molding in a Fontyne TP-400 press at 150 or 170°C for the times indicated.

Stress–strain properties were determined according to ISO 37, tear strength according to ISO 34/1, DIN abrasion ISO 4649, fatigue to failure ASTM 4482/85, and hardness according to ISO 48. Aging of the test specimens was carried out in a ventilated air oven at 100°C for 3 days (ISO 188). Heat buildup and permanent set after dynamic loading were determined using a Goodrich Flexometer (Load 11 or 22 kg; stroke 0.445 cm, frequency 30 Hz, start temperature 100°C) according to ISO 4666/3-1982. Dynamic mechanical analysis was carried out using an RDA-700 (prestrain 0.75%, frequency 15 Hz, and temperature 60°C) according to ASTM D 2231.

Vulcanizate network structure was determined by equilibrium swelling in toluene using the method reported by Ellis and Welding.¹⁰ The volume fraction (V_r) obtained was converted into the Mooney–Rivlin elastic constant (C_1) and finally into the concentration of chemical crosslinks by using equations described in the literature.^{11,12} The proportions of

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TABLE I
Truck Tire Tread Compounds

Ingredients	A, phr control	B, phr
NR SMR CV	80	80
BR Buna CB 10	20	20
Carbon black N-375	55	55
Zinc oxide	5.0	5.0
Stearic acid	2.0	2.0
Aromatic oil	8.0	8.0
6PPD	2.0	2.0
CBS	1.2	1.2
Sulphur	1.2	1.2
Perkalink 900	—	0.5

mono-, di-, and polysulphidic crosslinks in the vulcanizates were determined using thiol amine chemical probes.¹³ Following the cleavage of the poly- and di-sulphidic crosslinks, the samples were treated with methyl iodide to distinguish carbon-carbon-based crosslinks from monosulphidic crosslinks.^{14,15} Further details of the procedures have been reported previously.^{7,16,17}

The measurement of filler-polymer interaction has been determined according to the procedure described by Ayala et al.¹⁸ The interaction parameter I ($= \sigma/\eta$) is derived from both static and dynamic modulus measurements. The term σ is determined as the slope of the stress-strain curve in the relatively linear region, typically within the extension ratios ranging from 1 to 3. The higher the value, the greater the filler-polymer interaction. The term η is a measure of filler-filler networking, the so-called Payne effect, and is calculated from the difference in dynamic elastic modulus, G' , at 1% and 25% double-strain amplitude. The higher the value, the greater is the extent of

TABLE II
OTR Tread Compounds

Ingredients	C, phr	D, phr	E, phr	F, phr	G, phr
NR SMR 10	100	100	100	100	100
Carbon black N-220	40	40	40	40	40
Silica	20	20	20	20	20
Zinc oxide	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0	2.0
Aromatic oil	3.0	3.0	3.0	3.0	3.0
Coumarone resin	3.0	3.0	—	—	—
Colophonium resin	—	—	3.0	3.0	3.0
Coupling agent, TESPT	—	3.0	—	—	1.0
TMQ	1.5	1.5	1.5	1.5	1.5
6PPD	2.5	2.5	2.5	2.5	2.5
Wax	1.0	1.0	1.0	1.0	1.0
CBS	1.4	1.4	1.4	1.4	1.4
DPG	1.0	1.0	1.0	1.0	1.0
Sulphur	1.4	1.4	1.4	1.4	1.4
Perkalink 900	—	—	—	1.0	1.0

TABLE III
Cure Data at 150°C and Mooney Scorch

Properties	A	B
Delta torque, Nm	1.60	1.61
Scorch safety, ts2, min	5.5	5.4
Optimum cure time, t90, min	10.0	9.8
Mooney scorch, t5 (121°C), min	36	36

filler-filler networking thereby diminishing filler-polymer interaction.

RESULTS AND DISCUSSION

Truck tire tread compounds

The effect of Perkalink 900 in a typical truck tire tread compound (Table I, control) has been studied. The cure data presented in Table III clearly indicate that the antireversion agent is ineffective during the early stages of cure; scorch safety and time to optimum cure are unchanged. The material can thus be added to existing compounds with no further change in formulation, preferably during first stage mixing to ensure good dispersion.

Vulcanizate mechanical properties and heat buildup data are listed in Table IV. It is evident from the data that the antireversion agent stabilizes mechanical properties following extended cure, considered as an anaerobic aging process. In addition, heat buildup determined in the Goodrich Flexometer test is reduced considerably for the test compound containing Perkalink 900.

Viscoelastic properties are given in Tables V and VI. Perkalink 900 provides a benefit with regard to imparting some stability to tangent delta values following both anaerobic and oxidative aging. This suggests that the performance of a tread compound in terms of rolling resistance and heat buildup can be stabilized during the service life of the tire upon addition of the antireversion agent.

TABLE IV
Mechanical Properties Cured at 150°C/t90 and 60 Min
(Parentheses)

Properties	A	B
Modulus 100%, Mpa	2.4 (1.9)	2.5 (2.4)
Modulus 300%, Mpa	12.2 (10.3)	13.0 (12.5)
Tensile strength, Mpa	26.0 (22.5)	26.5 (24.5)
Elongation at break, %	550 (530)	530 (500)
Tear strength, kN/m	110 (75)	116 (90)
Abrasion loss, mm ³	95 (120)	90 (75)
Heat build up, ^a delta T, °C	52 (60)	40 (35)

^a Starting temp: 100°C, duration 30 min.

TABLE V
Viscoelastic Properties Cured at 150°C/t90 and 60 Min

Compounds	G', MPa	G'', MPa	Tangent Delta
A			
Cure t90	5.81	0.95	0.163
Cure 60 min	5.62	1.09	0.194
B			
Cure t90	5.90	0.95	0.161
Cure 60 min	5.84	0.99	0.170

OTR tire tread compounds

The objective of the study was again to evaluate the effect of the antireversion agent with regard to stabilizing vulcanizate hysteretic properties following aging. In addition, however, an attempt has been made to optimize the combination of the antireversion agent and the silane coupling agent, TESPT, with regard to providing improved performance at no cost penalty (compound G). The compound modifications are summarized as: C—as control but with no silane coupling agent, TESPT; D—control; E—as C but with colophonium resin in place of coumarone resin; F—as E with addition of Perkalink 900; G—as F with addition of silane coupling agent at reduced level.

The coumarone resin was replaced by colophonium because the antireversion agent is less effective in the presence of the former.⁹

Cure characteristics and Mooney viscosity are listed in Table VII and cure curves for compounds D and G in Figure 1. It is clear from the curves that the compound containing Perkalink 900 provides a striking improvement in reversion resistance compared to the control compound. The data presented in Table VII also indicate that compound G gives improved processing safety combined with reduced time to optimum cure, t90, suggesting that a faster cure can be achieved by the stock containing the Perkalink 900/TESPT combination.

Vulcanizate properties cured at 150°C/t90 and 60 mins are listed in Table VIII.

TABLE VI
Viscoelastic Properties Cured at 150°C/t90, Before and After Air Aging

Compounds	G', MPa	G'', MPa	Tangent delta
A			
Unaged	5.81	0.95	0.163
Aged 1day/100°C	6.25	1.18	0.190
Aged 3days/100°C	6.45	1.36	0.212
B			
Unaged	5.90	0.95	0.161
Aged 1day 100°C	6.20	1.05	0.170
Aged 3days/100°C	6.55	1.15	0.177

TABLE VII
Cure Characteristics at 150 and 170°C and Mooney Viscosity

Properties	D				
	C	control	E	F	G
Mooney visc. ML(1 + 4) 100°C, MU	94	85	87	87	85
Mooney scorch 121°C, min	16	10	19	19	16
Temperature 150°C					
Scorch safety, ts2, min	2.5	1.7	3.0	3.0	2.7
Optimum cure time t90, min	5.4	11.0	6.9	7.0	8.9
ML, Nm	0.23	0.25	0.25	0.23	0.25
Delta torque, Nm	1.55	1.85	1.56	1.53	1.82
Temperature 170°C					
Scorch safety, ts2, min	0.8	0.6	1.0	1.0	0.9
Optimum cure time t90, min	1.5	1.8	1.9	1.9	1.9
ML, Nm	0.19	0.23	0.23	0.21	0.23
Delta torque, Nm	1.40	1.63	1.51	1.48	1.63

As expected, eliminating TESPT from the control compound leads to a detrimental effect on all properties. Replacing the coumarone resin with colophonium resin (C and E, respectively) does not result in any significant change in properties with the exception of reduced heat buildup. The inclusion of the antireversion agent (compound F) leads to a further reduction in heat buildup, but not to the level of the control compound. However, the optimized compound, G, containing colophonium resin, 1 phr of TESPT, and 1 phr of Perkalink 900, exhibits similar modulus levels and heat buildup characteristics compared to the control compound. Furthermore, one major advantage shown by the optimized compound concerns blowout resistance on extended cure, as determined in the

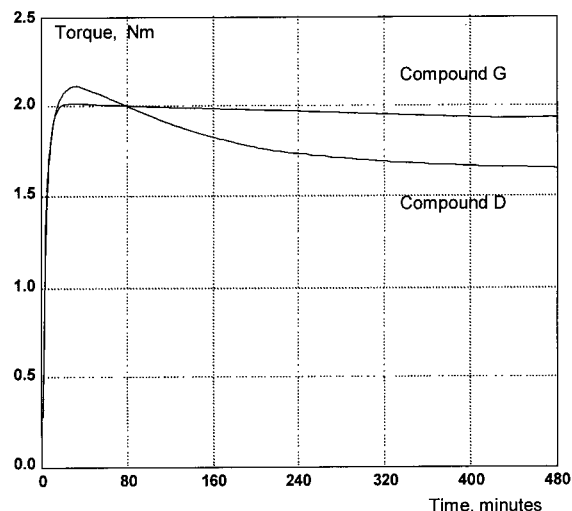


Figure 1 Cure curves at 150°C.

TABLE VIII
Vulcanizate Properties Cured at 150°C

Properties	Cure	C	D control	E	F	G
Hardness, IRHD	t90	73	77	75	75	79
	60'	68	76	72	75	79
Modulus 50%, MPa	t90	1.4	1.7	1.5	1.5	1.7
	60'	1.1	1.9	1.3	1.5	1.8
Modulus 100%, MPa	t90	2.5	3.4	2.7	2.6	3.2
	60'	1.8	4.0	2.2	2.6	3.7
Modulus 300%, MPa	t90	11.6	14.4	12.0	11.1	13.5
	60'	8.6	16.7	10.1	11.6	15.2
Tensile strength, MPa	t90	27.0	26.8	26.1	26.3	26.6
	60'	24.2	25.6	22.3	25.3	25.2
Elongation at break, %	t90	585	550	565	585	545
	60'	620	455	550	560	485
Tear strength, kN/m	t90	139	142	129	129	130
	60'	84	118	87	95	110
Heat build up at 100°C after 1 hour, $\Delta T^{\circ}\text{C}$	t90	55	25	45	38	27
	60'	55	24	45	28	24
Permanent set, %	t90	31	16	28	26	17
	60'	30	12	21	15	10
Fatigue to failure, k cycles (cam 14)	t90	150	181	145	165	180
	60'	181	168	nd ^a	nd	154
Abrasion loss, mm ³	t90	181	168	nd ^a	nd	154
	60'	186	171	nd	nd	158

^a Not determined.

Goodrich Flexometer test. The data are shown graphically in Figure 2.

A similar pattern in results is obtained when the vulcanizates are cured at 170°C/t90 and 30 min; the data are listed in Table IX.

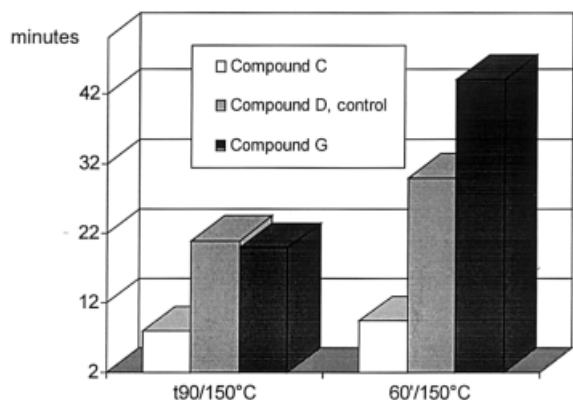


Figure 2 Goodrich flexometer blow-out time (100°C, load 216 N).

TABLE IX
Vulcanizate Properties Cured at 170°C

Properties	Cure	C	D control	E	F	G
Hardness, IRHD	t90	72	74	75	77	76
	30'	63	73	67	75	75
Modulus 50%, MPa	t90	1.4	1.7	1.5	1.5	1.7
	30'	0.9	1.6	1.1	1.3	1.6
Modulus 100%, MPa	t90	2.4	3.3	2.7	2.5	3.0
	30'	1.3	3.2	1.8	2.1	3.0
Modulus 300%, MPa	t90	10.9	13.9	11.9	10.8	12.9
	30'	6.3	14.5	8.0	9.9	12.9
Tensile strength, MPa	t90	26.7	26.4	26.3	26.2	26.6
	30'	18.8	23.7	17.2	23.0	23.4
Elongation at break, %	t90	590	535	565	585	560
	30'	615	485	520	565	510
Tear strength, kN/m	t90	125	140	129	123	150
	30'	40	80	85	73	80
Heat build up at 100°C after 1 hour, $\Delta T^{\circ}\text{C}$	t90	50	27	45	38	29
	30'	56	30	50	34	24
Permanent set, %	t90	28	21	29	29	25
	30'	31	15	28	17	11
Blow out time, min	t90	10	19	nd ^a	nd	17
	30'	7	25	9	23	43
Abrasion loss, mm ³	t90	190	170	nd	nd	155

^a Not determined.

Again, the compound containing the antireversion agent/TESPT combination, G, exhibits a similar performance compared to the control compound with the

TABLE X
Aged Stress/Strain Properties (3 Days/100°C) Cured at 150°C/t90 and 60 Min

Properties	Cure	C	D control	E	F	G
Modulus 50%, MPa	t90	1.9	2.7	2.0	2.3	2.6
	60'	1.6	2.5	1.7	2.1	2.5
Modulus 100%, MPa	t90	3.6	5.8	3.8	4.3	5.2
	60'	2.9	5.1	3.2	4.0	5.2
Modulus 300%, MPa	t90	14.2	19.1	14.2	15.6	17.7
	60'	12.1	18.2	12.4	15.3	18.0
Tensile strength, MPa	t90	22.4	23.1	21.4	22.8	23.8
	60'	20.1	20.8	18.7	21.1	21.6
Elongation at break, %	t90	495	415	470	460	440
	60'	490	350	455	430	380

TABLE XI
Viscoelastic Properties Determined at 60°C/15Hz/1% DSA

Compounds	Cure	G', MPa	G'', MPa	Tangent delta	% change in tangent delta ^a
C	t90/150°C	8.66	1.09	0.126	
	t90/170°C	7.51	1.04	0.138	
	30'/170°C	5.73	1.02	0.177	40
D, control	t90/150°C	8.23	0.97	0.118	
	t90/170°C	6.49	0.82	0.126	
	30'/170°C	7.01	1.02	0.145	23
G	t90/150°C	10.06	1.16	0.115	
	t90/170°C	9.53	1.17	0.125	
	30'/170°C	9.59	1.19	0.124	8

^a t90/150°C compared to 30'/170°C

added benefit of increased blow-out time on extended cure.

Table X records the aging behavior of the cured compounds in terms of stress-strain properties. Compounds D and G, containing 3 phr of TESPT and 1 phr TESPT/1 phr Perkalink 900, respectively, produce maximum modulus values during aging. However, retained tensile strength is not impaired compared to the other compounds that show reduced modulus buildup.

The viscoelastic properties of compounds C, D, and G are listed in Tables XI and XII. With regard to hysteresis loss expressed as tangent delta, both the presence of the silane coupling agent in the control compound and the combination with the antireversion agent in compound G provide some stability over the range of cure conditions (Table XI) and following aging (Table XII). However, it is compound G that exhibits the greater stability in tangent delta. Also, compound G maintains a higher level of elastic modulus, G'. These features should contribute to improved performance with regard to tire rolling resistance throughout its service life.

The reason for the greater stability in viscoelastic properties shown by the antireversion agent/ TESPT combination may lie in the stabilized network when considered in terms of crosslink densities. Total crosslink and crosslink type densities have been de-

termined for the three compounds in question cured at t90 and 8 h. Results are listed in Table XIII.

Compound C, containing no silane coupling agent, shows a fall in total crosslink density on overcure compared to the optimum cured network due to reversion. The control compound D shows a drop also, but not to the same degree as compound C; thus, TESPT can offer some degree of reversion resistance. This phenomenon has previously been reported and described in terms of an equilibrium cure system.¹⁹ However, compound G shows a negligible drop in total crosslink density through the formation of additional crosslinks based on a carbon-carbon structure, a result of its crosslink compensation mechanism.⁷ This crosslink compensation mechanism takes effect at the onset of reversion, either during overcure or during tire service.²⁰

The filler interaction parameters, σ and η , determined for the three compounds C, D, and G are listed in Table XIV. The data indicate that the elimination of TESPT (compound C compared to D) is detrimental to polymer-filler interaction, i.e., reduced σ , increased η . However, compounds D and G exhibit similar values for the interaction parameters, indicating that reinforcement characteristics remain essentially unchanged in the compound containing the TESPT/antireversion agent combination compared to TESPT

TABLE XII
Viscoelastic Properties Determined at 60°C/15Hz/1% DSA

Compounds	Cure	G', MPa	G'', MPa	Tangent delta	% change in tangent delta*
C, original	t90/150°C	8.66	1.09	0.126	
Aged 3 days/100°C		9.13	1.40	0.154	22
D, control original	t90/150°C	8.23	0.97	0.118	
Aged 3 days/100°C		10.51	1.42	0.136	15
G, original	t90/150°C	10.06	1.16	0.115	
Aged 3 days/100°C		10.97	1.32	0.121	5

* t90/150°C compared to aged 3 days/100°C

alone at a higher concentration. Moreover, compound G offers the added advantages of improved reversion resistance, more stable hysteretic properties and increased blow out resistance under conditions of overcure.

SUMMARY AND CONCLUSIONS

The effect of the antireversion agent Perkalink 900 has been studied in truck and OTR tread compounds, particularly with regard to stabilizing viscoelastic properties on overcure or following aging. In both compounds the antireversion agent provided benefits in this regard.

Perkalink 900 significantly improves reversion resistance by means of a crosslink compensation mechanism: the replacement of reverted polysulphidic crosslinks by thermally stable crosslinks based on a carbon-carbon structure. Crosslink density measurements provide evidence for this.

The antireversion agent in combination with TESPT at a reduced level in the silica containing OTR compound gives improved performance with regard to the stability of viscoelastic properties, blow-out resistance and reversion resistance at no cost penalty.

TABLE XIII
Crosslink density and Distribution of Crosslink Types—
Cure 150°C/t90 and 8 H (Parentheses)

Crosslink density ^a	C	D control	G
Total crosslinks	4.75 (3.27)	5.46 (4.42)	5.32 (5.20)
Polysulphidic	2.31 (0.70)	3.01 (1.21)	2.91 (1.30)
Disulphidic	0.27 (0.30)	0.69 (0.52)	0.62 (0.55)
Monosulphidic	2.17 (2.27)	1.76 (2.69)	1.79 (2.59)
Carbon-Carbon based	0 (0)	0 (0)	0 (0.76)

^a Crosslink density expressed in gram mol/g rubber hydrocarbon $\times 10^5$.

TABLE XIV
Polymer-Filler Interaction Parameter I—Cure 150°C/t90

Compounds	σ ($M_{300} - M_{100}$)	η ($G_{\max} - G_{\min}$)	I = (σ/η) $\times 10^2$
C	9.1	780	1.16
D, control	11.0	430	2.55
G	10.4	425	2.45

These benefits may help to improve the performance of heavy duty tires with regard to rolling resistance and heat buildup throughout their service life.

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