

Effect of Antiozonants on Rubber-to-Metal Adhesion

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Part 1

Introduction

Diene elastomers like natural rubber (NR) and polybutadiene (BR) are commonly used in dynamic applications such as tires, belts, isolators, and dampers. Diene rubber vulcanizates contain free double bonds which are sensitive to attack by oxygen and ozone. Natural rubber, polybutadiene, and blends thereof are usually formulated with active antiozonants, both to protect against the degrading effects of ozone and to improve the resistance to fatigue in dynamic applications. At least one study has shown that antiozonants, particularly 77PD, cause a decrease in rubber-to-metal adhesion values^[1]. This study included plasticizers, antidegradents, accelerators, and two levels of sulfur. Because of the wide use of antiozonants in bonded mounts and the potential adhesion reducing impact of including them in the formulation, a more detailed study of the effect of antiozonants was undertaken.

Methodology

The two test methods used for adhesion testing were ASTM D 429 Method B coupons and Method F buffer specimens. A generic natural rubber/polybutadiene formulation was chosen for the study with all compound variants being approximately 55 to 60 durometer. For the first portion of the study, two solvent-based adhesive systems and one water-based adhesive system were chosen. All three systems employed a primer and an adhesive covercoat. The two solvent-based adhesives represent first and second generation technologies. The water-based adhesive system represents newly-developed third generation technology. The first generation solvent-based adhesive system is identified as "Cover 1" and the second generation solvent based adhesive system is identified as "Cover 2". The water-based adhesive system is simply referred to as "Aqueous". Commercially available materials were used in compounding the formulations used in this study. In all cases, the compounds contained:

Ingredient	phr
Natural Rubber CV60	75.0
High cis polybutadiene	25.0
Zinc Oxide	5.0
Stearic Acid	1.0
2,2,4-Trimethyl-1,2-dihydroquinoline polymer (TMQ)	1.0
N650 Carbon Black	45.0

The first two studies used a cure system consisting of:

Ingredient	phr
Sulfur	2.5
N-cyclohexyl-2-benzothiazole sulfenamide (CBS)	0.7
N-(cyclohexylthio) phthalimide	0.2

The compounds were mixed in a BR1600 lab Banbury using the following mix procedure:

First Cycle

0 seconds	load natural rubber
30 seconds or 80°C	load polybutadiene and 1/2 black
100°C	load 1/2 black and chemicals
115°C	sweep
125°C	sweep
135°C	dump

Second Cycle

0 seconds	load first cycle masterbatch and curatives
30 seconds or 95°C	sweep
60 seconds or 105°C	dump

All antidegradents were added in the first cycle while sulfur and accelerators were added in the second cycle. Final dispersion was accomplished on a 15 x 30 cm two-roll mill. Testing was performed per the following test methods:

Hardness	ASTM D 2240
Tensile, elongation and modulus	ASTM D 412 Method A
Adhesion	ASTM D 429 Method F or Method B

The Method F buffer test was chosen as the primary test because it is representative of the geometry of many parts. Method B peel specimens were also tested in the second study because they are commonly used throughout the industry. The Method B peel test was run at the allowed 45° angle instead of the standard 90° angle. According to the ASTM procedure, "Experience indicates a lower force is obtained for the 45° than for the 90° angle, and also a break significantly closer to the bond surface." Method F buffer specimens were cured to 90% of rheometer cure (Tc90) plus 5 minutes via injection molding. Method B peel specimens were cured to Tc90 cure time plus 10 minutes via compression molding. The metal components were 1020 cold rolled steel which were zinc phosphatized prior to primer and adhesive application. The primers and adhesives were prepared for use following the instructions given on the technical data sheets for the respective products. Primers and adhesives were applied by spray. The primers were applied at dry film thicknesses between 7.5-12 microns. Adhesives were applied at dry film thicknesses between 15-19 microns.

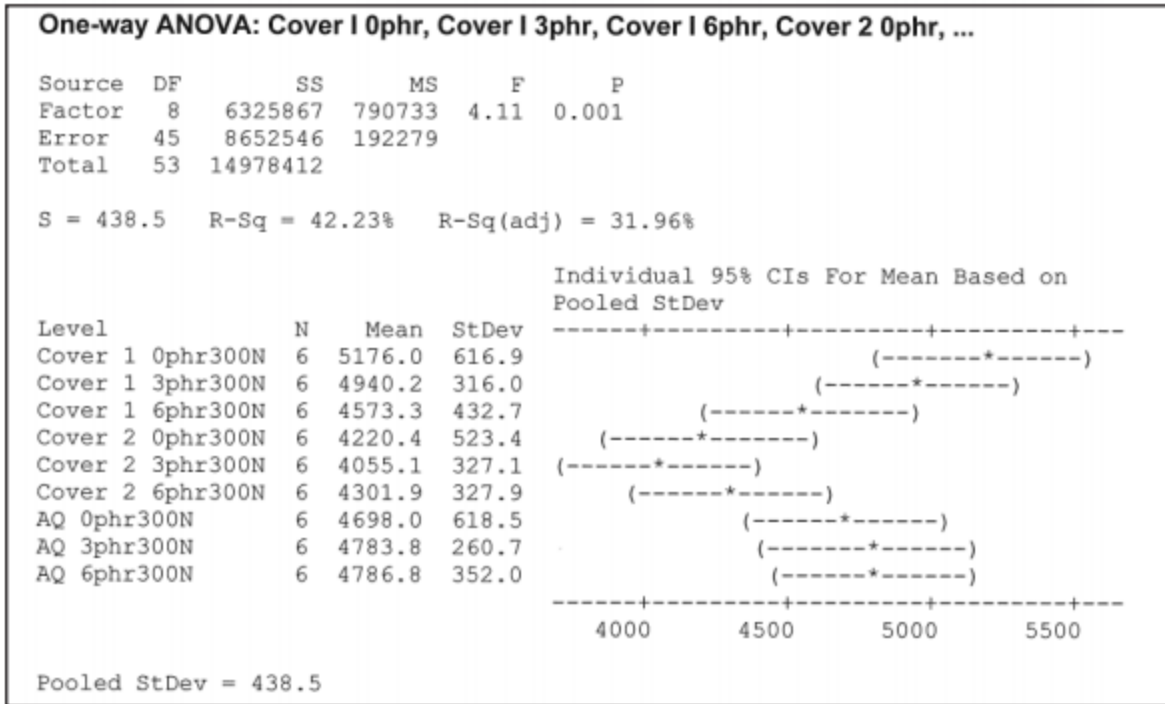
Results

The first study investigates the use of N-1,3-Dimethylbutyl-N'-phenyl-p-phenylene diamine or Santofl ex 6PPD, a commonly used antiozonant. This was incorporated at three different levels and molded at two different temperatures (150°C and 170°C) using the three selected adhesive systems. Method F buffer specimens were used for this study. Table 1 shows the antiozonant type and levels and the results of the testing while Tables 2 and 3 show the statistical analysis of the adhesion tests. One-way unstacked analysis of variance (ANOVA) was the statistical analysis tool used in all the studies. The confidence level chosen for the analysis was 95%. The statistical analysis shows a drop in adhesion at 150°C when using the Cover 1 adhesive system as the level of 6PPD antiozonant increases from 0 to 6 phr. There is no significant impact when using either Cover 2 or the Aqueous adhesive systems. At 170°C cure temperature, none of the adhesive systems were negatively impacted by the addition of 6PPD. The percentage of retained rubber was statistically insignificant between all the conditions. The second study investigated a number of commonly used antiozonants at the high level of 6 phr. Since the Cover 1 adhesive system showed the most sensitivity to antiozonant loading, these antiozonants were evaluated using only the Cover 1 adhesive and molding was performed only at 150°C. Method F and Method B specimens were used for this study. Table 4 shows the antiozonant type and the results of the testing while Table 5 shows the statistical analysis of the adhesion tests.

Table 1 – Results for 6PPD at three different levels

Compound	1	2	3
6PPD antiozonant (phr)	0.00	3.00	6.00
Properties			
Rheometer @ 150°C (MDR)			
ML Low torque	1.94	1.90	1.88
MH High torque	15.77	15.21	14.88
Tc90 (minutes)	12.96	12.68	12.42
Ts2 (minutes)	6.75	6.67	6.61
Hardness (Shore A)	58	57	57
Tensile (MPa)	24.7	23.4	22.9
Elongation (%)	580	585	585
100% modulus (MPa)	2.5	2.4	2.2
Adhesion Test Method F Zinc-Phosphatized Buffers			
Molded at 150°C			
Cover 1 average (newtons)	5176	4940	4573
Rubber retained (%)	96	98	96
Cover 2 average (newtons)	4220	4055	4301
Rubber retained (%)	89	88	92
Aqueous average (newtons)	4698	4784	4787
Rubber retained (%)	82	96	96
Molded at 170°C			
Cover 1 average (newtons)	5192	4782	4822
Rubber retained (%)	100	97	99
Cover 2 average (newtons)	4308	4220	4289
Rubber retained (%)	99	100	99
Aqueous average (newtons)	4281	4599	4867
Rubber retained (%)	67	100	97

**Table 2 – ANOVA chart for study 1 (0, 3, 6 phr antiozonant with Cover 1, Cover 2, and Aqueous adhesive)
Molding @ 150°C**



**Table 3 – ANOVA chart for study 1 (0, 3, 6 phr antiozonant with Cover 1, Cover 2, and Aqueous adhesive)
Molding @ 170°C**

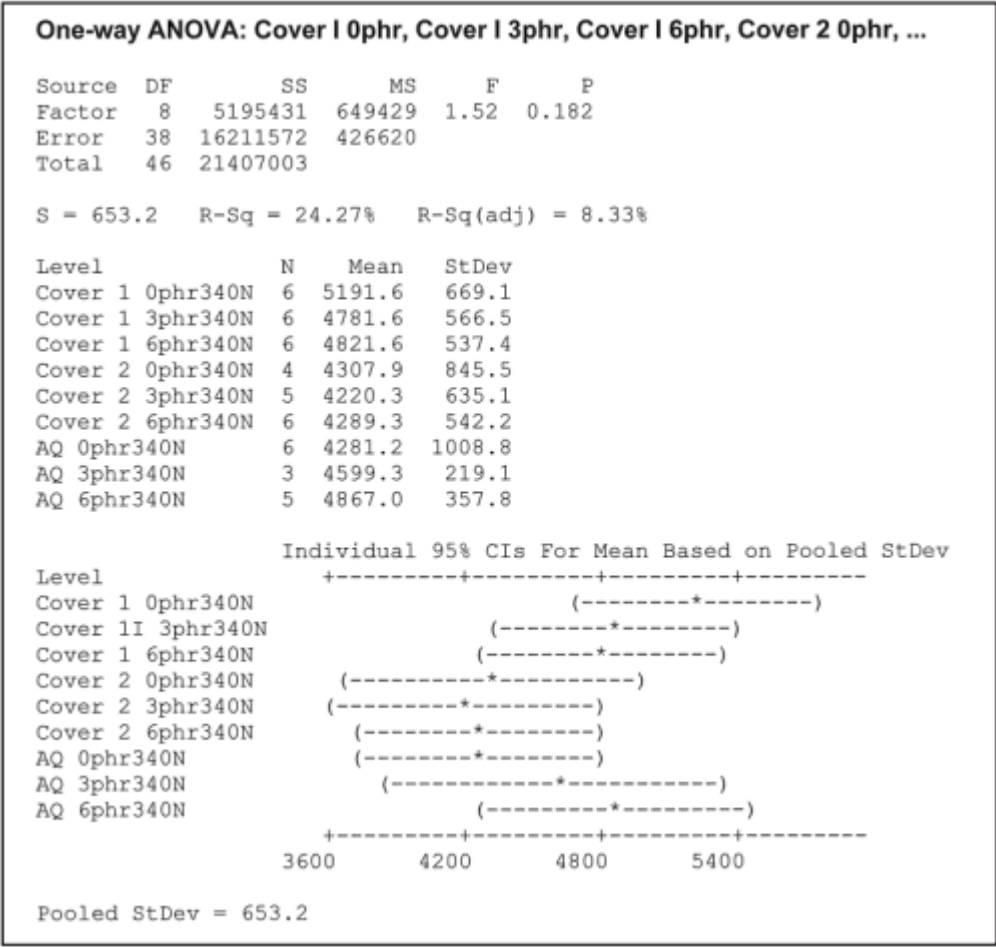
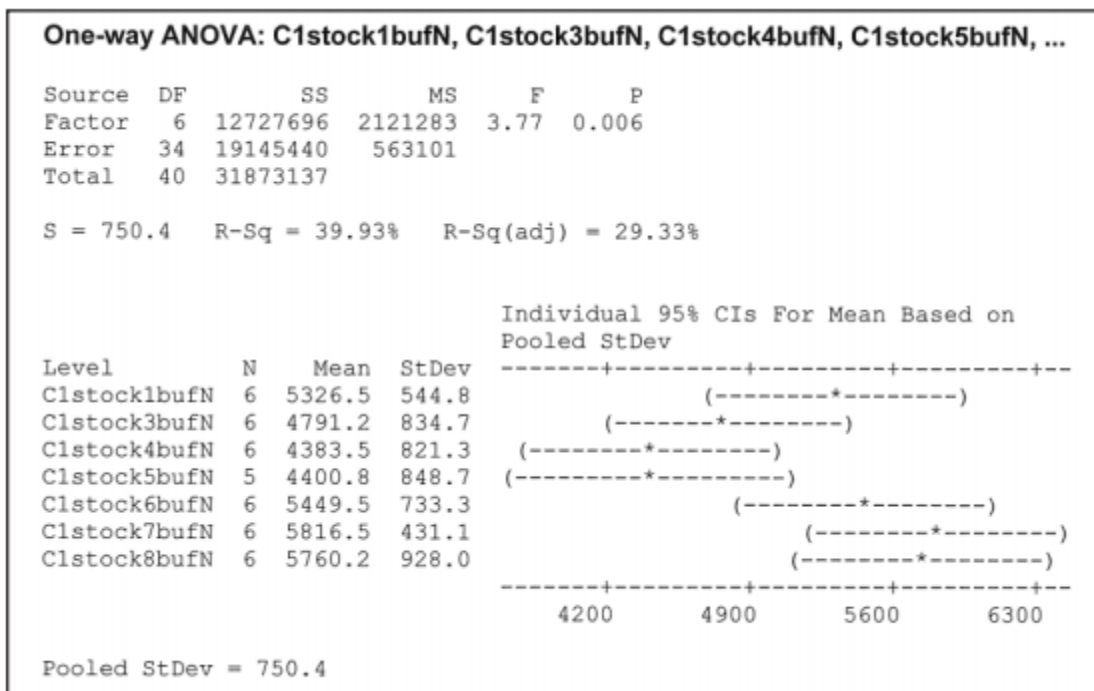


Table 4 – Comparative results for six different antiozonants

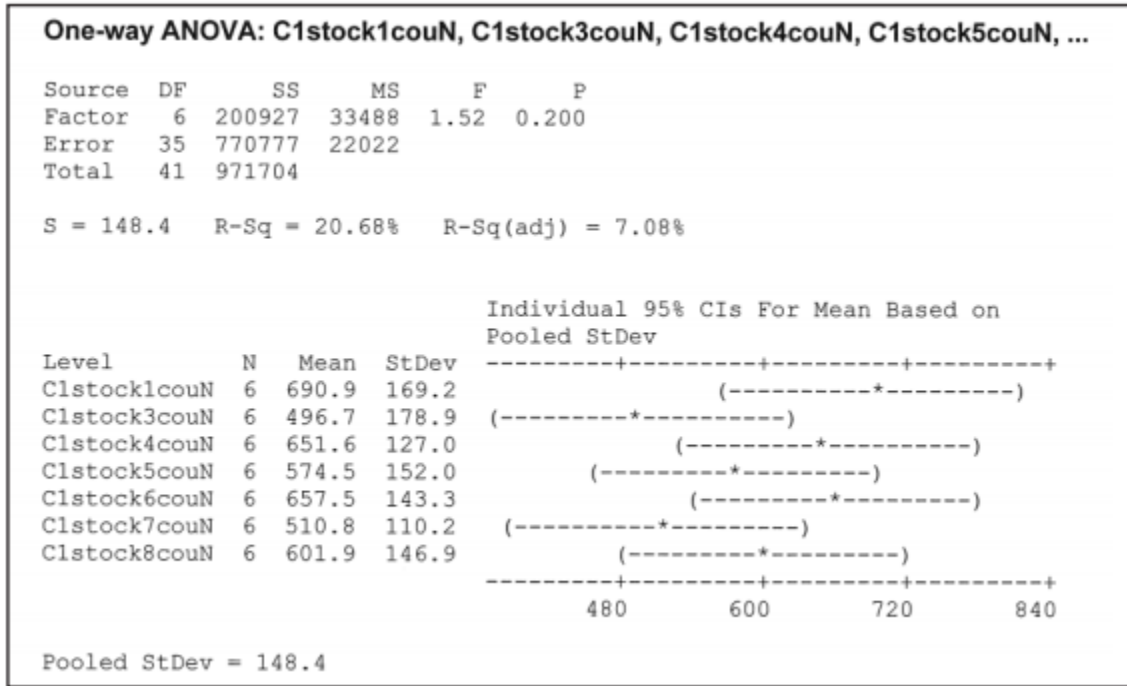
Compound	1	3	4	5	6	7	8
6PPD	—	6.00	—	—	—	—	—
IPPD	—	—	6.00	—	—	—	—
77PD	—	—	—	6.00	—	—	—
PPD Blend (Flexzone 11L)	—	—	—	—	6.00	—	—
Substituted 1,3,5 Triazine	—	—	—	—	—	6.00	—
TMQ	—	—	—	—	—	—	6.00
Properties							
Rheometer @ 150°C (MDR)							
ML Low torque	1.94	1.88	1.84	1.84	1.83	1.77	1.85
MH High torque	15.77	14.88	14.78	14.52	14.59	14.34	13.89
Tc90 (minutes)	12.96	12.42	11.38	10.63	12.32	12.55	12.41
Ts2 (minutes)	6.75	6.61	5.96	5.43	6.28	6.67	6.24
Hardness (Shore A)	58	57	55	54	57	56	58
Tensile (MPa)	24.7	22.9	23.0	21.9	23.2	23.3	23.0
Elongation (%)	580	585	590	565	580	620	610
100% modulus (MPa)	2.5	2.2	2.2	2.3	2.4	2.2	2.2
Adhesion Test Method F Zinc-Phosphatized Buffers							
Molded at 150°C							
Cover 1 average (newtons)	5326	4791	4384	4401	5450	5816	5760
Rubber retained (%)	96	92	88	95	84	83	89
Adhesion Test Method B Zinc-Phosphatized Coupons							
Cover 1 average (newtons)	691	497	652	574	658	511	602
Rubber retained (%)	100	100	100	100	100	100	100

Table 5 – ANOVA chart for different antiozonants in NR (Cover 1 adhesive) Molding @ 150°C; on buffers



Most of the antiozonants chosen are either dialkyl or alkyl-aryl para-phenylene diamines. Two commonly used antiozonants are N-IsopropylN'-phenyl-p-phenylenediamine (IPPD) and N,N'- Bis(1,4-dimethylpentyl)-p-phenylenediamine (77PD). A proprietary blend of para-phenylenediamines sold under the trade name of Flexzone® 11L was included in the investigation. One chemically different antiozonant investigated was a substituted triazine, specifically 2,4,6-Tris-(N-1,4-dimethylpentyl-p-phenylenediamino)- 1,3,5-triazine sold under the trade name of Durazone® 37. As a further control, 6 phr of TMQ was added to Compound 8 in addition to the 1 phr TMQ that was included in all formulations. While TMQ is primarily used as an antioxidant, it is known to have some limited antiozonant properties. The statistical analysis of adhesion data on Method F buffer specimens shows that compounds 4 and 5 containing IPPD and 77PD have the most pronounced negative effects on adhesion. There is no significant impact from TMQ, Flexzone 11L or Durazone 37. As in the first study, differences in the percentages of retained rubber were insignificant. As part of this evaluation, Method B coupon adhesion specimens were also evaluated to determine if the same trends could be observed with a different type of specimen. The statistical analysis is shown in Table 6. Although the buffer test showed clear differences, the scatter in the coupon test was so great that there were no statistically significant differences. This may simply mean that coupon tests lack the precision to be able to discern the differences.

Table 6 – ANOVA chart for different antiozonants in NR (Cover 1 adhesive); Molding @ 150°C; on coupons

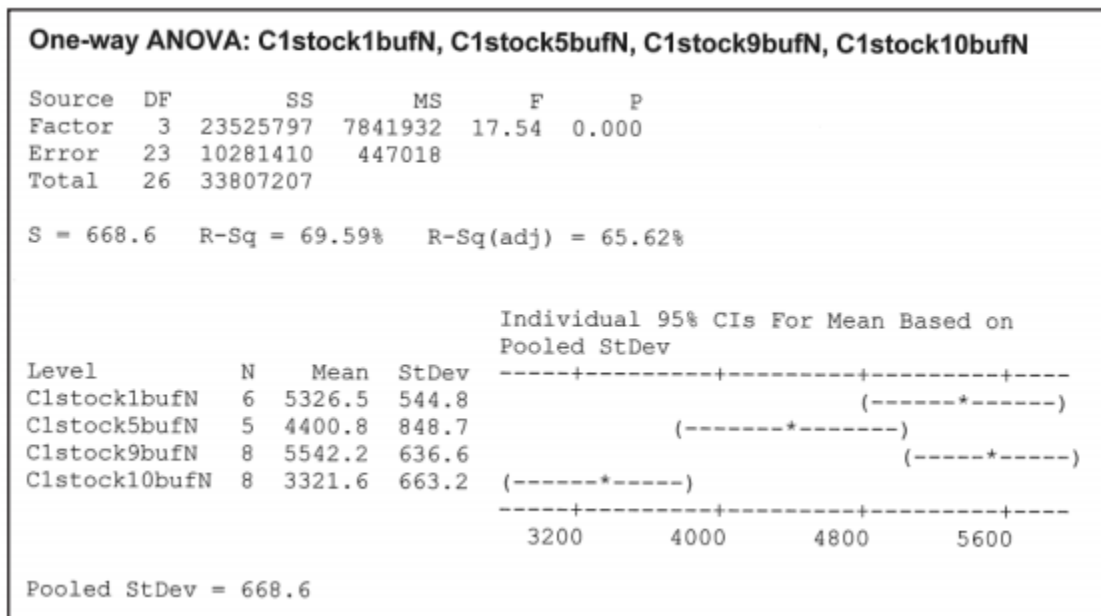


It is possible that the high sulfur cure system chosen is responsible for reducing the impact of the antiozonant choices. To evaluate this hypothesis, a third experiment was run using a low sulfur cure system for comparison. To make the comparison relevant, the same accelerator was used in both compounds (Table 7). The statistical analysis of the Method F buffer adhesion data (Table 8) shows clearly that the low sulfur cure system is significantly more sensitive to the presence of the 77PD antiozonant than the high sulfur cure system. In this experiment, we see a large drop in the pull values for the low sulfur cure system that contains the 77PD antiozonant. There were significant differences in the percentage of retained rubber between the high sulfur cure system and the low sulfur cure system.

Table 7 – High and low sulfur cure systems with 77PD

Compound	1	5	9	10
77PD	—	6.00	—	6.00
Sulfur	2.50	2.50	0.70	0.70
CBS	0.70	0.70	2.50	2.50
PVI	0.20	0.20	0.20	0.20
Properties				
Rheometer @ 150°C (MDR)				
ML Low torque	1.94	1.84	2.17	2.01
MH High torque	15.77	14.52	13.98	11.80
Tc90 (minutes)	12.96	10.63	13.43	6.55
Ts2 (minutes)	6.75	5.43	9.08	3.80
Hardness (Shore A)	58	54	55	50
Tensile (MPa)	24.7	21.9	22.9	23.2
Elongation (%)	580	565	555	655
100% modulus (MPa)	2.5	2.3	2.1	2.4
Adhesion Test Method F Zinc-Phosphatized Buffers				
Molded at 150°C				
Solvent 1 average (newtons)	5326	4265	5542	3321
Rubber retained (%)	96	92	68	56

Table 8 – ANOVA chart for high and low sulfur cure systems with 77PD



Summary & Conclusions

1. Adhesion is affected by the choice of adhesive system, the choice and level of the antiozonant, and by the choice of cure system in the rubber compound.
2. At lower curing temperatures, some adhesive systems are more sensitive to the presence of 6PPD antiozonant than other adhesive systems. At higher curing temperatures using a high-sulfur cure system, these differences are indistinguishable.
3. Of the antiozonants tested, IPPD and 77PD showed the greatest effect on adhesion followed by 6PPD. The other antiozonants tested had no measurable impact on adhesion when using a high-sulfur cure system.
4. Method B coupon tests may be less discerning than Method F buffer tests to differences in adhesion.
5. The low sulfur cure system is significantly more sensitive than the high sulfur cure system to the presence of the 77PD antiozonant. The addition of 77PD causes a significant loss in the bond strength.