



*Producers of Specialty Chemicals*

**Struktol Company of America**

201 E. Steels Corners Road • P. O. Box 1649 • Stow, Ohio 44224-0649

STP0239  
Paper # 56

## Improving Silane Coupling to Rubber The Use of a Zinc Processing Additive

John Vander Kooi  
Struktol Company of America

Rubber Division ACS  
Oct 5-8, 2004  
Columbus, OH  
ISSN: 1547-1977

([jvanderkooi@struktol.com](mailto:jvanderkooi@struktol.com))

## **Abstract:**

Examination of the silanes used by the tire industry from the bifunctionality of the silane (TESPT and TESP) shows that both silanol and sulfur chemistry can be addressed. The sulfur crosslinking reaction is shown to be influenced by the presence of zinc chemicals in silica containing NR formulations. The use of a selected zinc containing chemical, ZB 47, designed for sulfur modification of the silane, is shown. Mixing, processing, curing, and dynamic properties are all influenced by synergism seen between the zinc material and the silane. These results suggest that improved dispersion and filler to rubber crosslinking efficiency are achieved.

## **Introduction:**

The use of the alkoxy silanes bis (triethoxysilylpropyl)tetrasulfide (TESPT) and bis (triethoxysilylpropyl) disulfide (TESPD) to modify rubber properties when mineral fillers are compounded has been of great commercial interest for several decades. (1, 2) This field is still extremely active. Currently (July 2004) the US patent office has the key word listing of 66 applications for TESPT and 22 for TESP (using only the initials for the search). The work of Rauline (2), using a 3 pass mix with solution polymers, has become the standard for a passenger tread with improved dynamic properties. There has developed mixing procedures where bases such as zinc oxide are delayed during the initial silica silane reaction period(3,4). It is thought that the zinc components react with the silica surface, which decreases hydrophobation with the silanol. The emphasis of these works has been on the silane and silanol reaction path ways. It appears that much of the conclusions about these reactions are tempered by the presence of water or the molar limitation of water present during mixing(5,6). After the silanols have condensed on the silica surface the sulfur portion of the silane is envisioned to be available for reactions with the vulcanization system to tie the filler to the rubber. (Fig 1).

Zinc chemistry (7) and the control of concentration and the structure of the fatty acids used is an important variable in the vulcanization process(8). Mechanisms that use expanding d orbitals of the zinc ligand complexes have been used to explain this role of zinc(9). The TESPT has a polysulfide chain with S ranking of about 3.8. The TESP has a nominal S ranking of slightly more than 2. From a vulcanization stand point the polysulfide should be easily incorporated into reactive coupling intermediates. It should make sulfur available for normal crosslinking as well as coupling. It is more problematical that the disulfides would incorporate easily in coupling intermediates. In the disulfide little sulfur will become free to join the sulfur pool. In fact, interesting compounding changes are required for substitution of TESPT by TESP(4). When combining the issues of zinc interactions with silica/silanols and vulcanization chemistry along with the complexities of mixing, this system is extremely complicated in physics and chemistry. In this work a NR compound with mixed fillers based on CB and silica treated with TESP in a 2 pass mix was treated with a zinc soap compound, ZB. This material is a proprietary blend of fatty acid derivatives. The material contains 10% zinc. The additives were all added during the 1<sup>st</sup> pass, which should give the most problems with non productive interactions.

## **Experimental:**

Compound recipe. The formulations tested are shown in Table 1. The variations tested were a control with no silane or added ZB. The silane was added at 5% level of the silica (Si) and ZB was added at 2.5 and 5 phr(2.5ZB and 5ZB).

The N220 was obtained from Harwick Standard. The silica was from Degussa. Struktol A 86 is a peptizer and 40MS is a resin and Struktol SCA 985PL is a 50% pelletized TESP. The other ingredients are standard rubber additives.

The compounds were mixed in a Farrel BR 1600 lab mixer at 77 rpm with a 70% fill factor in a two pass process. In the 1<sup>st</sup> pass the NR was mixed with the peptizer for 40 secs and the rest of the ingredients were added. The 1<sup>st</sup> of 2 sweeps was made after 90 secs and the total mix time was 240 secs. The curatives were added in a 2<sup>nd</sup> pass which was 80 secs.

Standard testing done on the stocks included Mooney viscosity (ASTM D 1646), cure rheometer (ASTM D 2084), tensile testing (ASTM D 412), rebound (ASTM D 2632), and dynamic testing (ASTM D 623). Cured viscoelastic testing was done in compression using a Mechanical Energy Resolver (MER-1100B) manufactured by Instrumentors, Inc.

## **Discussion:**

The combination of the silane TESP and the zinc ZB shows both processing and physical property synergism. The mixing curves show that most of the processing improvements came from the addition of ZB. There is faster incorporation and significantly lower mixing torques. There is a concentration dependence on the mix. (Fig 2-5 ). Depending on mixing criteria suggests that mixing times and work inputs could be significantly reduced with the zinc compound. In this work it is not possible to compare whether the influence of the additive is strongest on one filler or the other. The shape of the mixing curve and the faster incorporation peaks implies better uniformity and dispersion with the combination of additives. The drop temperatures are high enough to obtain a decent level of silanization.

Secondary processing steps also were more influenced by the zinc compound. The Mooney viscosity (Fig 6) shows large changes for the initial viscosity. The long term storage viscosity showed a storage effect of an increase in ML (1+4) of over 120 for the control and the silane while the ZB containing stock only increased 5 units. Although limited extrusion trials (cold feed) were done, the aged stock showed a 20 % reduction in torque for the silane and a 25% reduction for the silane and ZB combination. A similar drop in pressure was seen with no change in output rate at fixed RPM. The surface and edge rating went from B6 to A9 with the combination. These results suggest that filler flocculation is not occurring in the presence of the ZB additive but is occurring with the silane alone(10).

Both the silane and the zinc compound influenced the scorch delay. The best scorch was with the combination at the high level of zinc. The cure time was also extended slightly

(Fig 7). Some of the reversion resistance of these compounds comes from the silane and zinc chemical but most is obtained with the combination (Table 2 ).

The efficiency of the crosslinking , as measured by 100% modulus, shows that silane contributes more than the zinc chemical. However, the combination has the highest state of cure. (Table 3) Oxidative aging shows a lower % change for the combination. (Table 4 ) Tear resistance is maintained (Fig 8 ).

The dynamic properties as measured by rebound (Table 5), shear (Table 6 ), and compression (Table 7 ) all show significant synergism between the silane and the ZB. The biggest change is seen in the long term dynamic distortion on the Firestone Flexometer were the combination was shut off before the sample failed. All these results are consistent with each other and with better filler dispersion and coupling efficiency.

### **Conclusion:**

The combination of processing effects and physical properties of this type of NR coupled silica show that significant improvements can be made by the use of zinc chemistry. Although this work does not answer whether the coupling of silica to rubber is enhanced by an increased efficiency of the silane sulfur to enter into the vulcanization mechanism it does suggest that this does occur. It also suggests that more work is required to understand why the viscosity of the zinc enriched systems did not show significant storage hardening effects.

### **References:**

- 1 US Patent 3,873,489, F. Thurn et.al. (Degussa)
- 2 US Patent 5,227,425, R. Rauline, (Michelin)
- 3 L. Reuvekamp, S. Debnath, J. Ten Brinke, P. Van Swaaij, J. Noordermeer, Rubber Chem and Tech , Vol 76, 34, 2003
- 4 C. Stone, K. Menting, M. Hensel, ACS Rubber Division Meeting, Oct. 2000, #59
- 5 K.J. Kim, J. Vanderkooi, J.Appl. Polym. Sci. (to be published)
- 6 K.J. Kim, J Vanderkooi, ACS Rubber Division Meeting, Oct. 2003, #78
- 7 G. Heideman, J. Noordermeer, R. Datta, Rubber Chem and Tech, Vol 77, 336, 2004
- 8 US Patent 5,302,315, H. Umland, (Schill & Seilacher)
- 9 J. Vanderkooi, J. Sherritt, H. Umland, M. Hensel, ACS Rubber Division Meeting, Oct. 1993, #121
- 10 A. Hasse, A Wehmeier, H.-D. Luginsland, Rubber World 230, #1, 22, 2004

**Acknowledgement: Kevin Tracy, Barb Eickelberry, and K.J. Kim assisted in the generation of the data and format of this presentation.**

Figure 1

## Reaction Intermediate

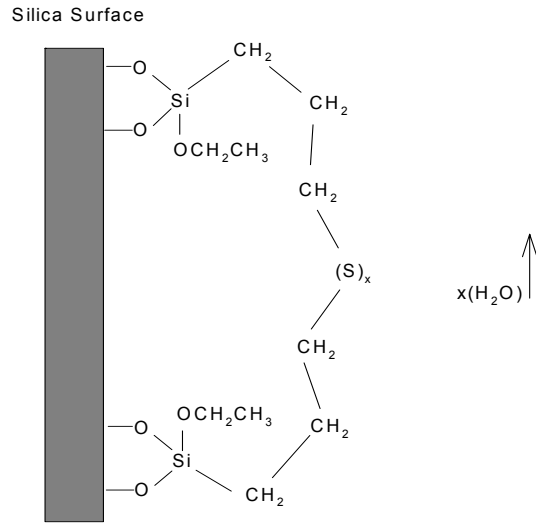


Figure 2

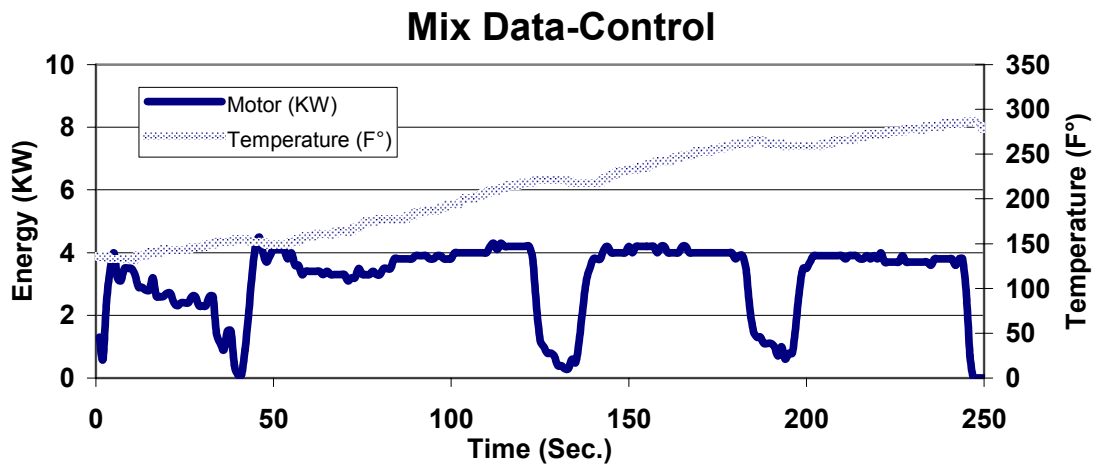


Figure 3

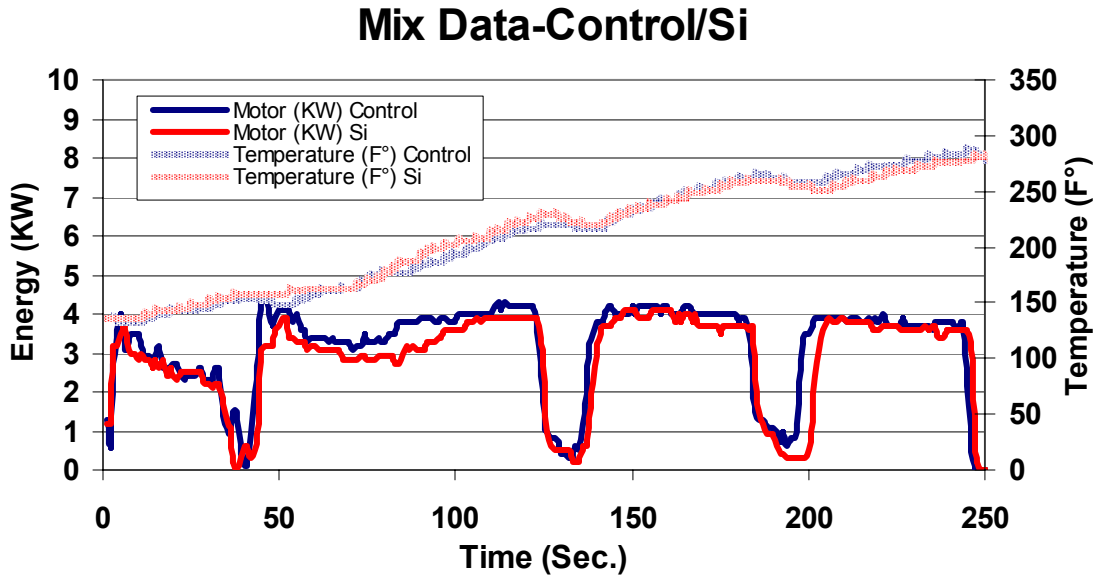


Figure 4

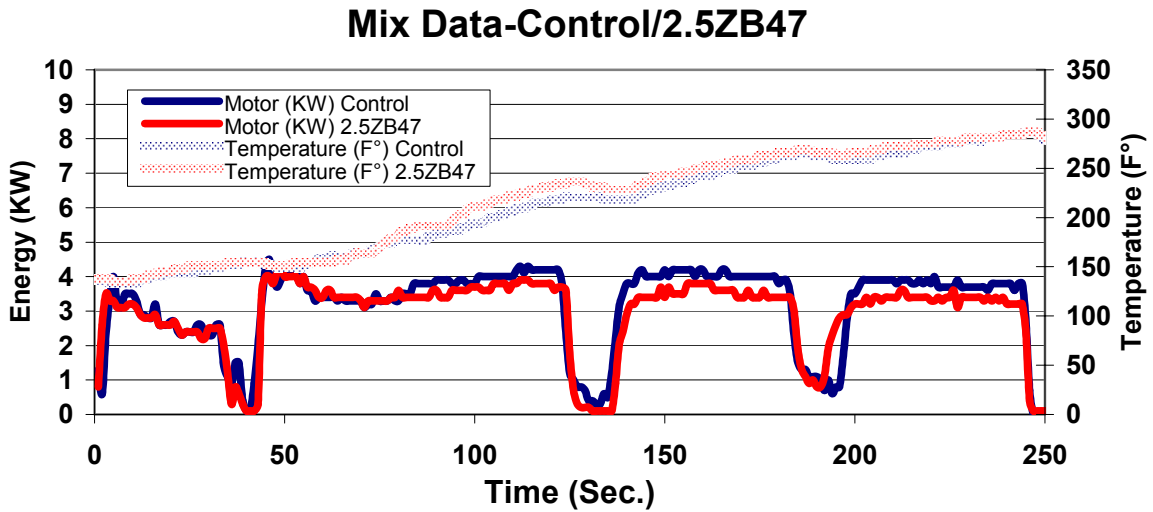


Figure 5

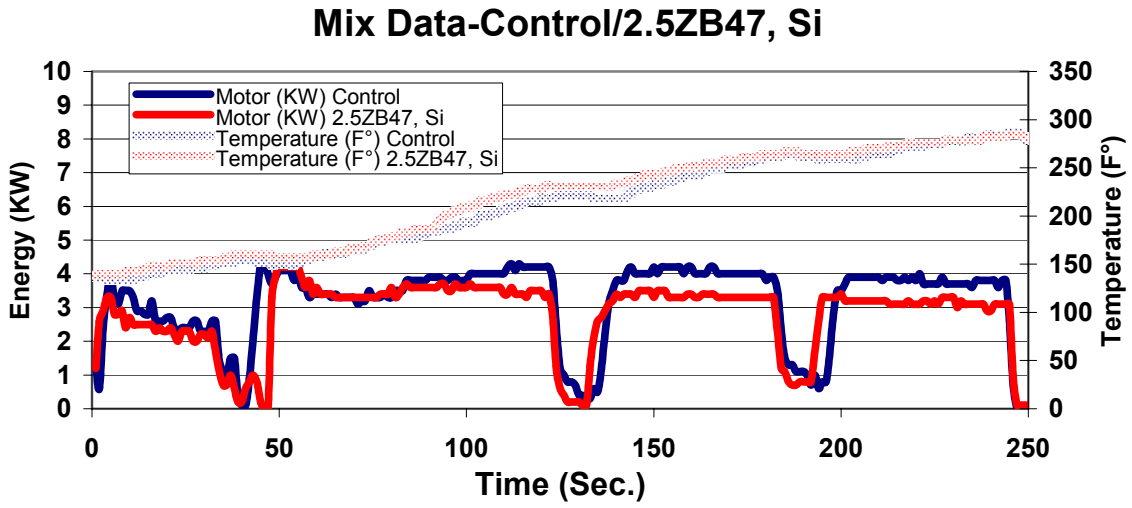


Figure 6

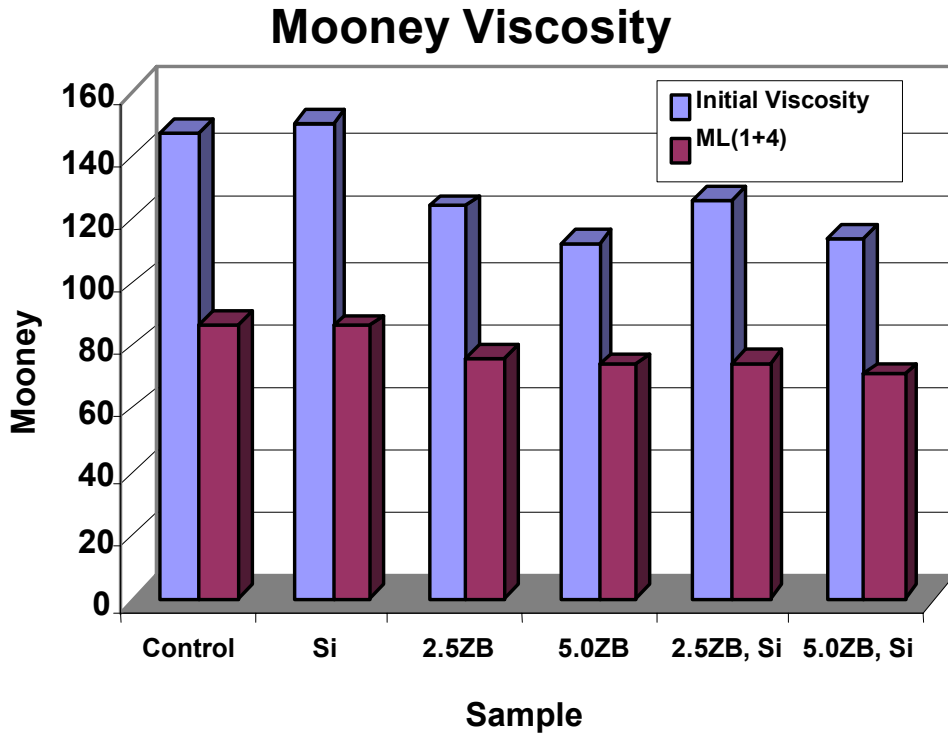


Figure 7

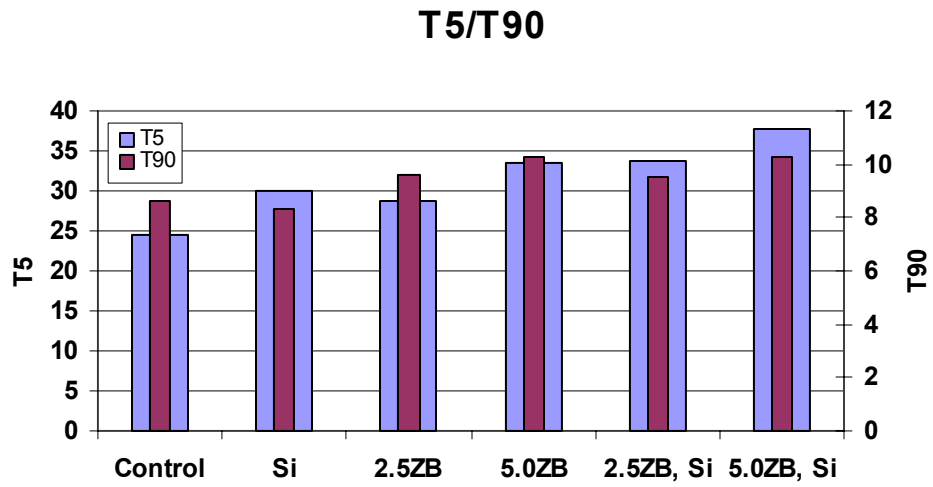


Figure 8

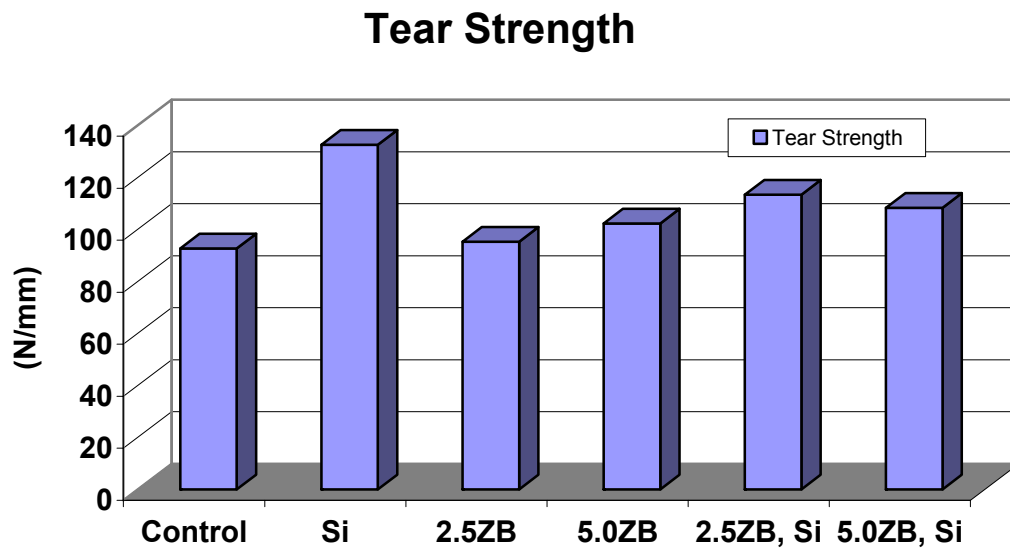




Table 1

## Formulations

Ingredient	-	Si	2.5ZB	5.0ZB	2.5ZB, Si	5.0ZB, Si
SMR 5	100	100	100	100	100	100
A 86	.25	.25	.25	.25	.25	.25
N220	40	40	40	40	40	40
Silica VN3	20	20	20	20	20	20
Stearic Acid	2.5	2.5	2.5	2.5	2.5	2.5
ZnO	4	4	4	4	4	4
6PPD	2.5	2.5	2.5	2.5	2.5	2.5
TMQ	1	1	1	1	1	1
Struktol 40MS	6	6	6	6	6	6
SCA985PL	0	2	0	0	2	2
ZB47	0	0	2.5	5	2.5	5
2 <sup>nd</sup> Pass						
TBBS	1.5	1.5	1.5	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5
<b>Total</b>	<b>179.25</b>	<b>181.25</b>	<b>181.75</b>	<b>184.25</b>	<b>183.75</b>	<b>186.25</b>

Table 2

## Reversion

Compound	T-2 Reversion
Control	13.29
Si	13.71
2.5ZB	15.29
5.0ZB	18.00
2.5ZB, Si	18.00
5.0ZB, Si	25.92

Table 3

## Modulus Data

<b>Compound</b>	<b>100% Modulus (Mpa)</b>	<b>300% Modulus (Mpa)</b>	<b><u>300% Modulus</u> 100% Modulus</b>
<b>Control</b>	1.6	8.1	5.1
<b>Si</b>	2.0	9.8	4.9
<b>2.5ZB</b>	1.8	8.3	4.6
<b>5.0ZB</b>	1.7	7.6	4.5
<b>2.5ZB, Si</b>	2.1	9.8	4.7
<b>5.0ZB, Si</b>	2.3	10.2	4.4

Table 4

## Aged 70 Hrs. @ 100°C

<b>Compound</b>	<b>%Change 100% Modulus</b>	<b>%Change 300% Modulus</b>
<b>Control</b>	106	69
<b>Si</b>	90	55
<b>2.5ZB</b>	117	82
<b>5.0ZB</b>	100	72.3
<b>2.5ZB, Si</b>	90	54.1
<b>5.0ZB, Si</b>	78.2	47

Table 5

## Rebound

<b>Compound</b>	<b>0°C</b>	<b>Room Temp.</b>	<b>100°C</b>
<b>Control</b>	18	35	50
<b>Si</b>	16	34	53
<b>2.5ZB</b>	16	33	51
<b>5.0ZB</b>	15	33	52
<b>2.5ZB, Si</b>	17	34	54
<b>5.0ZB, Si</b>	15	32	55

Table 6

## Firestone Flexometer Heat Build-Up and Blowout

250lb. Weight; .325" throw. Heat Build-up 45min.

Blowout run until machine proximity switch activates.

<b>Compound</b>	<b>Heat Build-up (C°)</b>	<b>Blow-Out (Min.)</b>
<b>Control</b>	164	65
<b>Si</b>	129	680
<b>2.5ZB</b>	141	230
<b>5.0ZB</b>	139	882
<b>2.5ZB, Si</b>	133	>6180
<b>5.0ZB, Si</b>	127	>8631

**Table 7**

## Tan Delta

	<b>Room Temp.</b>		<b>100°C</b>	
<b>Compound</b>	<b>1Hz</b>	<b>10Hz</b>	<b>1Hz</b>	<b>10Hz</b>
<b>Control</b>	.163	.165	.131	.134
<b>Si</b>	.135	.132	.112	.113
<b>2.5ZB</b>	.167	.164	.152	.143
<b>5.0ZB</b>	.149	.147	.119	.121
<b>2.5ZB, Si</b>	.145	.147	.102	.108
<b>5.0ZB, Si</b>	.131	.141	.095	.103