Paper C12

Quantifying Subtle Differences Among Different Grades of Zinc Oxide Used Commercially in the Rubber Industry

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Abstract

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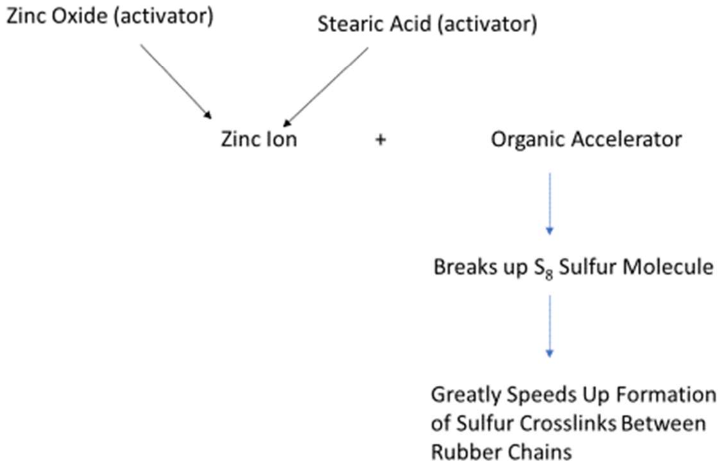
Zinc oxide is used as the main activator along with stearic acid in the vast majority of rubber formulations today. However, some have considered zinc oxide as just another industrial chemical. On the other hand, we in ASTM D11 spent many years characterizing different grades of zinc oxide in relation to their performance in various rubber compounds and the establishment of at least three new ASTM Standards developed in the 1990's for judging the zinc oxide quality and general suitability in various rubber compounds. This paper carries this work further by comparing these different grades of zinc oxide in critical rubber compounds.

INTRODUCTION

Most rubber compounds used today contain zinc oxide as the preferred activator.

Traditionally zinc oxide is used in most sulfur cured rubber compounds as an activator to promote three-dimensional crosslinking which yields a vulcanizate with unique dynamic properties. This is illustrated in Figure 1 below.[1]

Figure 1



In addition, zinc oxide is important in achieving good steel tire cord adhesion as has been demonstrated by Alex Peterson.[2]

Zinc oxide is also used as an activator of blowing agents, such as OBSH, which are commonly used in closed cell sponge rubber compounds as shown by Ralph Annicelli.[3]

ASTM Studies

Because of the importance of characterizing performance differences among different Zinc Oxide Grades, we established several task groups under ASTM D11 Main Committee on Rubber to develop such standards.[4,5,6]

From the task group work performed under ASTM D11.20 Sub-Committee on Rubber Compounding Materials, we developed three important standards between 1979 and 1989 for characterizing different grades of zinc oxide.

ASTM D4315 describes all the ASTM test methods that were established and approved for characterizing different grades of zinc oxide. These are shown in Figure 2 below.

Figure 2

ASTM D4315

Standard ASTM Test Methods for Testing Zinc Oxide for Use in Rubber Compounding

- % Zinc Oxide
- Concentration of Lead and Cadmium
- Determination of Sulfur in Zinc Oxide
- % Heat Loss
- Surface Area
- % Sieve Residue

Also, ASTM D4295 was developed in the same time period to classify the different grades of zinc oxide that are currently used in the rubber industry. These are shown in Figure 3 below.

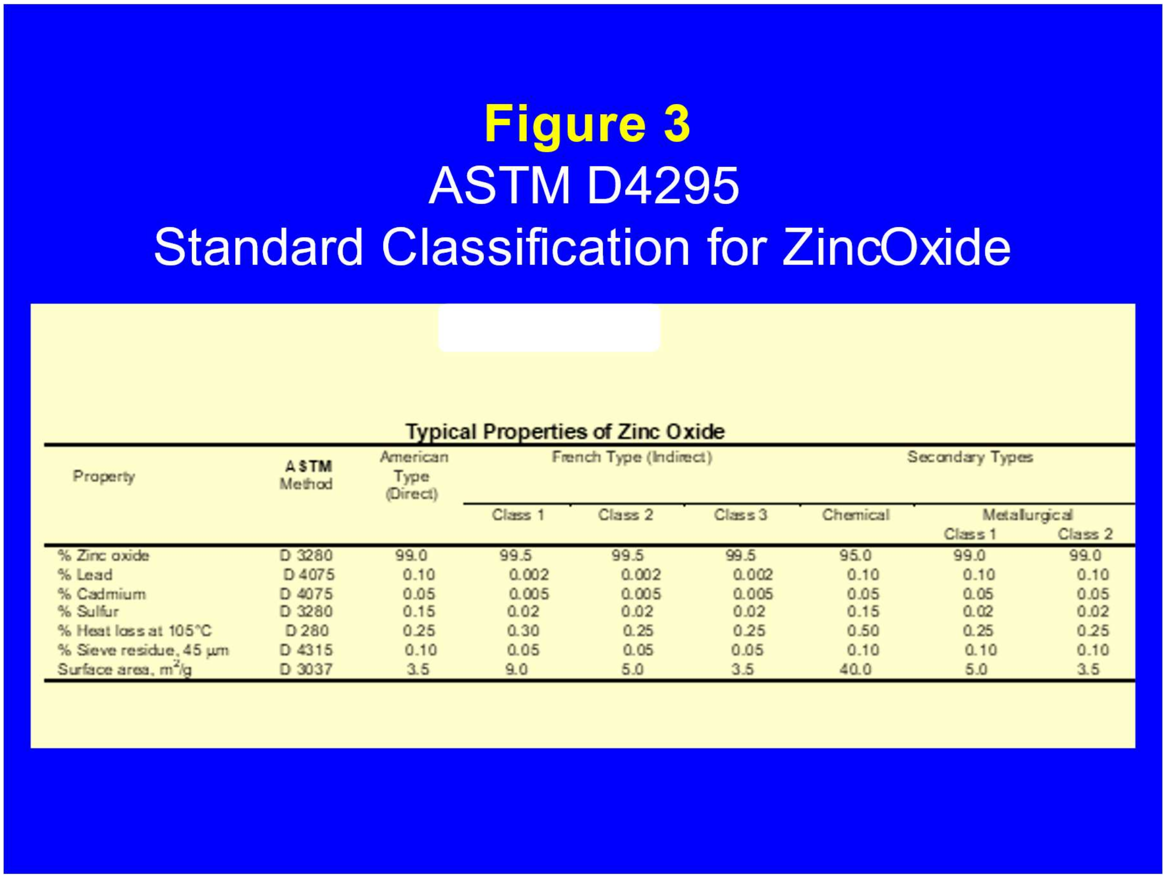


Figure 3

ASTM D4295

Standard Classification for ZincOxide

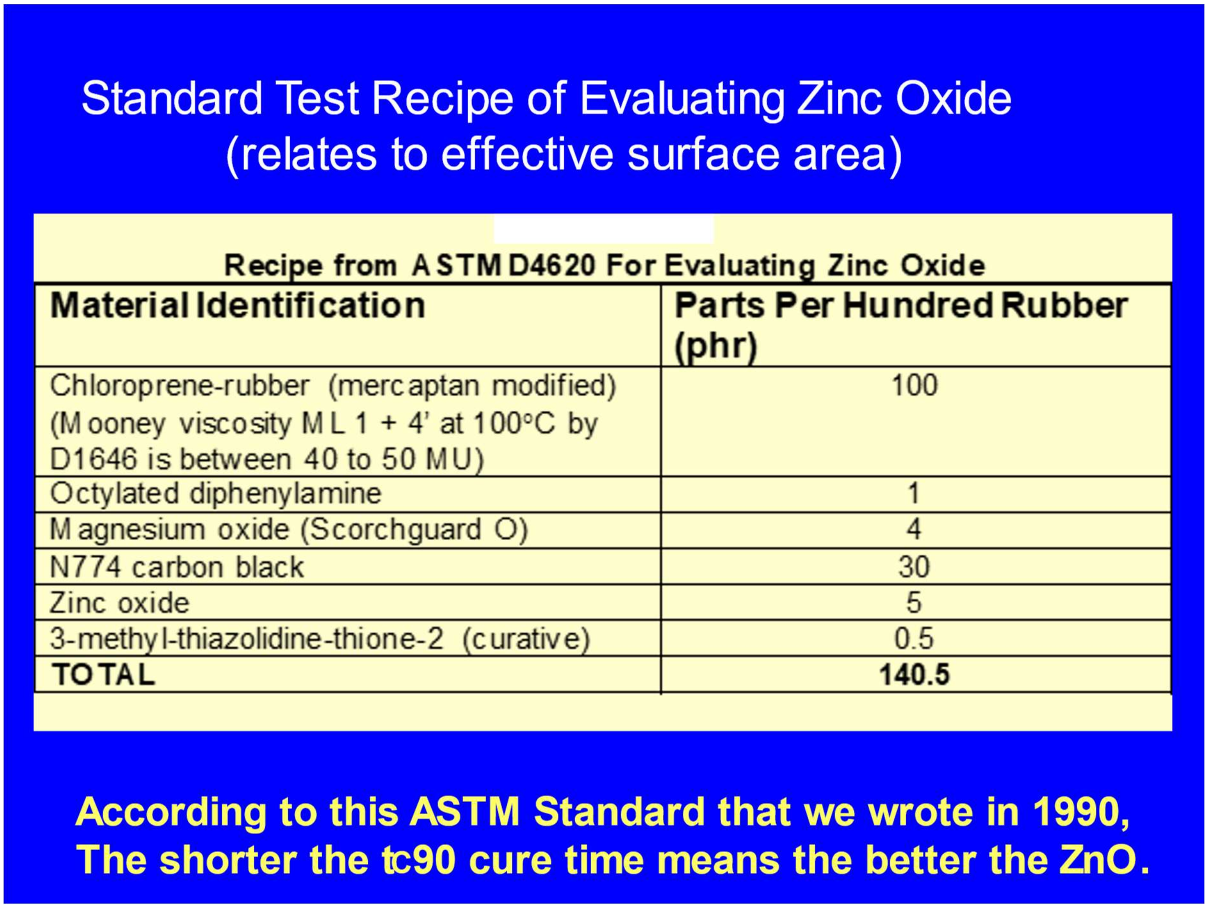
Typical Properties of Zinc Oxide

Property	**ASTM** Method	American Type (Direct)	French Type (Indirect)			Secondary Types		
			Class 1	Class 2	Class 3	Chemical	Metallurgical Class 1	Metallurgical Class 2
% Zinc oxide	D 3280	99.0	99.5	99.5	99.5	95.0	99.0	99.0
% Lead	D 4075	0.10	0.002	0.002	0.002	0.10	0.10	0.10
% Cadmium	D 4075	0.05	0.005	0.005	0.005	0.05	0.05	0.05
% Sulfur	D 3280	0.15	0.02	0.02	0.02	0.15	0.02	0.02
% Heat loss at 105°C	D 280	0.25	0.30	0.25	0.25	0.50	0.25	0.25
% Sieve residue, 45 µm	D 4315	0.10	0.05	0.05	0.05	0.10	0.10	0.10
Surface area, m^2/g	D 3037	3.5	9.0	5.0	3.5	40.0	5.0	3.5

As can be seen from Figure 3, there are a total of seven different ASTM grades of zinc oxide used in the rubber industry. In the author's opinion, surface area, purity, and % lead and cadmium content are some of the most important zinc oxide tests. Certainly, the available surface area for a given zinc oxide grade in square meters per gram is very important in predicting its performance in a rubber compound.[7] Also, typically the aspect ratios of the particles of zinc oxide grades that come from American Process (Direct process) vs. the French Process (Indirect process) are different.

In addition, ASTM D4620 was developed during this same time period as a more effective way of measuring the chemical reactivity and available surface area of a grade of zinc oxide by simply measuring the time-to-cure (t_C90). The shorter the t_C90 means the higher the available surface area per weight of the zinc oxide. As described earlier, zinc oxide is the most common activator used with various rubbers to activate the cure by chemically interacting with accelerators. However, with rubber compounds based on halogenated elastomers such as Neoprene, zinc oxide is actually the crosslinking agent.[8] This is why our ASTM Task group created this neoprene recipe given below in Figure 4 to be used to evaluate selected zinc oxide samples.

Figure 4



Standard Test Recipe of Evaluating Zinc Oxide (relates to effective surface area)

Recipe from ASTM D4620 For Evaluating Zinc Oxide

Material Identification	**Parts Per Hundred Rubber (phr)**
Chloroprene-rubber (mercaptan modified) (Mooney viscosity ML 1 + 4' at 100°C by D1646 is between 40 to 50 MU)	100
Octylated diphenylamine	1
Magnesium oxide (Scorchguard O)	4
N774 carbon black	30
Zinc oxide	5
3-methyl-thiazolidine-thione-2 (curative)	0.5
TOTAL	**140.5**

According to this ASTM Standard that we wrote in 1990,
The shorter the tc90 cure time means the better the ZnO.

Lastly in our ASTM work around 1990, we developed ASTM D5900 which gives the specifications for the ASTM IRM 91 Zinc Oxide, Industrial Reference Material, which is shown below in Table 1.

Table 1

Specifications for IRM 91 Zinc Oxide

Property	**ASTM Test Designation**	**Limits / Targets**
Surface Area m2/g	D4315 and D3037	4.3±0.3
% Zinc oxide	D3280	99.5 min.
% Lead	D4075	0.08 max.
% Cadmium	D4075	0.08 max.
Heat Loss @ 105°C %	D280	0.50 max.
Wet Sieve Analysis, % retains on 45 µm	D4315	0.10 max.

IRM 91 is commonly used in various ASTM standard recipes published in the ASTM International 2021 Annual Book of ASTM Standards. Through ASTM D11 (Committee on Rubber), one can purchase small quantities of IRM 91 zinc oxide from a current inventory of 1700 lb. for laboratory evaluations. Some find IRM 91 makes for an excellent "control" in evaluating different grades of zinc oxide that are currently available in the rubber industry.[9]

Experimental

The purpose of this study is to find the most sensitive physical tests for quantifying subtle differences in performance among the wide range of different grades of commercial zinc oxide that are regularly used by the rubber industry today. After much discussion and review, it was decided to use three specific recipes which are shown below.

1. The ASTM D4620 Neoprene Recipe (shown in Figure 4)
2. A typical tire "wire coat adhesion compound"
3. The latest generation silica tread compound

The zinc oxide samples that we tested are as follows:

1. **Control** - A French Process Zinc Oxide with Surface area of 5.2 m^2/g
2. **Half Control** -only half the concentration of the "control" used (in order to measure sensitivity of the specific compound to changes in concentration of the zinc ion)
3. **AP** – An American Process Zinc Oxide with a surface area of 1.8 m^2/g
4. **CB** – Commercial blend of Zinc Oxide commonly used, with a surface area of 4.0 m^2/g

The goal of this study is to determine whether or not performance differences among these four zinc oxide samples can be seen when used in the three different compounds listed above with the appropriate physical testing program.

Neoprene Study (ASTM D4620)

The compound shown in Figure 4 was laboratory mill mixed in accordance with the ASTM D4620 procedure. The "order of mix" used on the lab mill is given below.

MILL MIXING DETAIL

Roll Temperature: 50°C

Band Polymer: 60 Sec.

Add Zinc Oxide

Add Magnesium Oxide

Add Antioxidant

Add Carbon Black

Add Curative

Cross Cut 3 times each direction

Cigar 6 times

Sheet off

Approximate mix time 12 – 15 minutes

Tire Wire Coat Compound

The model tire wire coat formulation used in this study is given below.

Figure 5

Tire
Belt
Skim
Coat
Compound

Ingrediants	Name	phr
NR	CV60	100.00
Carbon Black	N326	55.00
Silica	Z1085	8.00
Activator	Zinc Oxide	6.00
Activator	Stearic Acid	1.50
Plasticizer (Paraffinic)	Sunpar 150	2.00
Antiozonant	6PPD	1.00
Antioxidant	TMQ	1.00
Methylene Acceptor	B20	2.75
Cobalt Salt	Cobalt Neodecanoate 22.5 + Boron	0.40
Accelerator	DCBS	1.00
Methylene Donor	Cyrez 963	3.00
Curative	HS OT 20 Sulfur	5.00
TOTAL		186.65

Wire Coat Skim compound addition order:

Stage 1 Mix

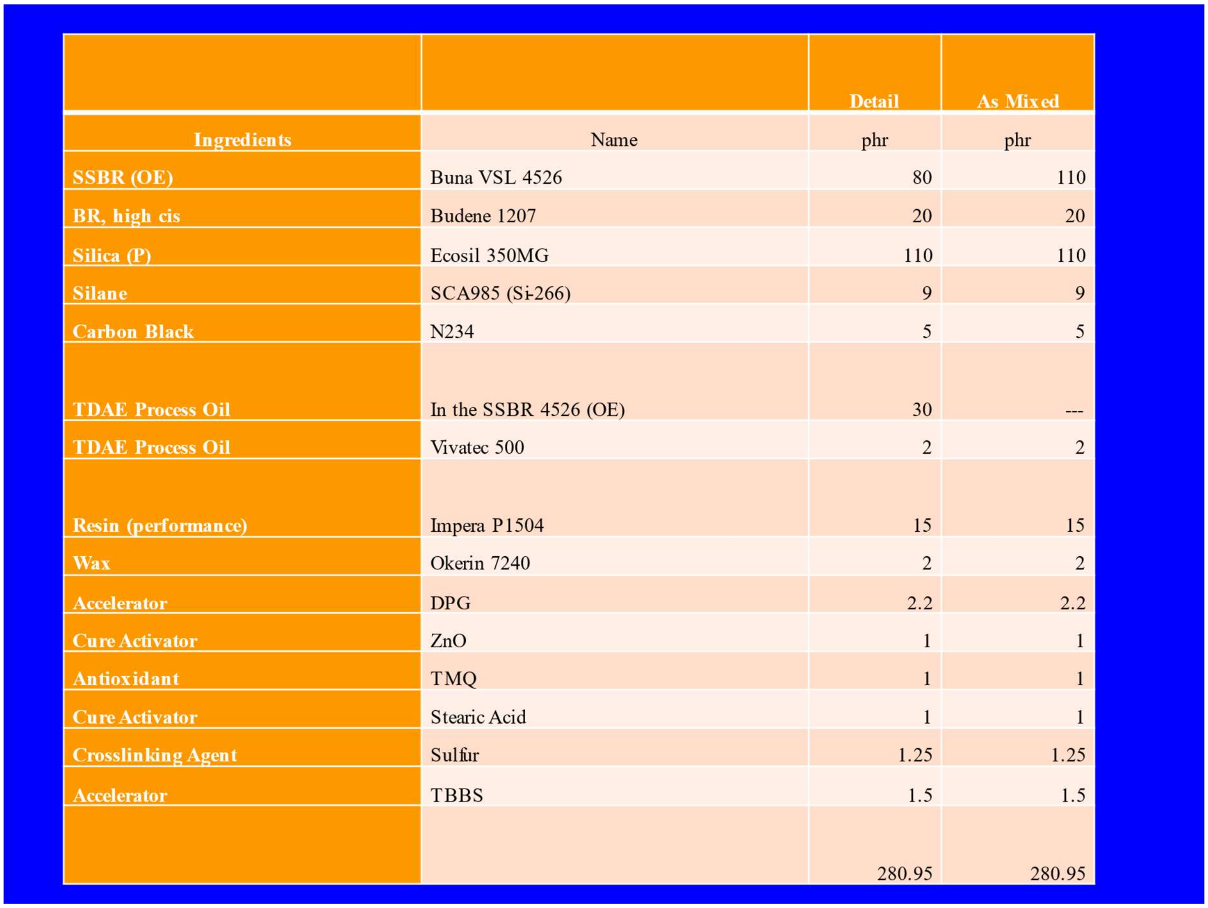
- Natural Rubber
- Carbon Black
- Silica
- Zinc Oxide

    Stearic Acid
    Paraffinic oil: Sunpar 150
    6PPD
    TMQ
    Methylene Acceptor (B20 or B19)
Stage 2 Mix
    Remill Masterbatch 1
Stage 3 Mix
    Cobalt Salt: Cobalt Neodecanoate 22.5%
Stage 4 Mix (Productive)
    Accelerator DCBS
    Methylene Donor: Cyrez 963
    Sulfur

The New 3rd Generation of Low Rolling Resistance Silica Treads

The model recipe for the latest experimental New Generation of Low Tire Rolling Resistant Silica Tread that was used in this study is shown below:

Figure 6



		Detail	As Mixed
Ingredients	Name	phr	phr
SSBR (OE)	Buna VSL 4526	80	110
BR, high cis	Budene 1207	20	20
Silica (P)	Ecosil 350MG	110	110
Silane	SCA985 (Si-266)	9	9
Carbon Black	N234	5	5
TDAE Process Oil	In the SSBR 4526 (OE)	30	---
TDAE Process Oil	Vivatec 500	2	2
Resin (performance)	Impera P1504	15	15
Wax	Okerin 7240	2	2
Accelerator	DPG	2.2	2.2
Cure Activator	ZnO	1	1
Antioxidant	TMQ	1	1
Cure Activator	Stearic Acid	1	1
Crosslinking Agent	Sulfur	1.25	1.25
Accelerator	TBBS	1.5	1.5
		280.95	280.95

This experimental silica has a total of **110 phr** precipitated hydrated silica which required multiple passes to achieve dispersion. This new recipe is very difficult to mix and actually required six lab passes.

Table 2 shows the order of addition:

Table 2

Stage 1: Masterbatch mix sequence	Add polymers
	Add 50 phr Silica + Silane
	Add 35 phr Silica
	Add 25 phr Silica
	Add other Ingredients: carbon black, oil, wax, resin
	Adjust rotor speed to increase mix temperature. Hold temperature to promote silica/silane hydrophobation reaction: 160-165°C / 320-329°F for 3+ minutes.
	Dump. Transfer to RT mill with 6 knife flips and 6 pig rolls
Stage 2 (remill) mix	Add all masterbatch #1
	Dump at 3.5 minutes
	RT mill with knife flips for 1 minute
Stage 3 (non-productive) mix	Add masterbatch #2, DPG, ZnO, TMQ
	Dump at 3.5 minutes
	RT mill with knife flips for 1 minute
Stage 4 (productive) mix	Add 1/2 masterbatch #3
	Add sulfur, stearic acid, TBBS in MB #3 pocket
	Dump at 2.5 minutes
	RT mill with knife flips for 1 minute

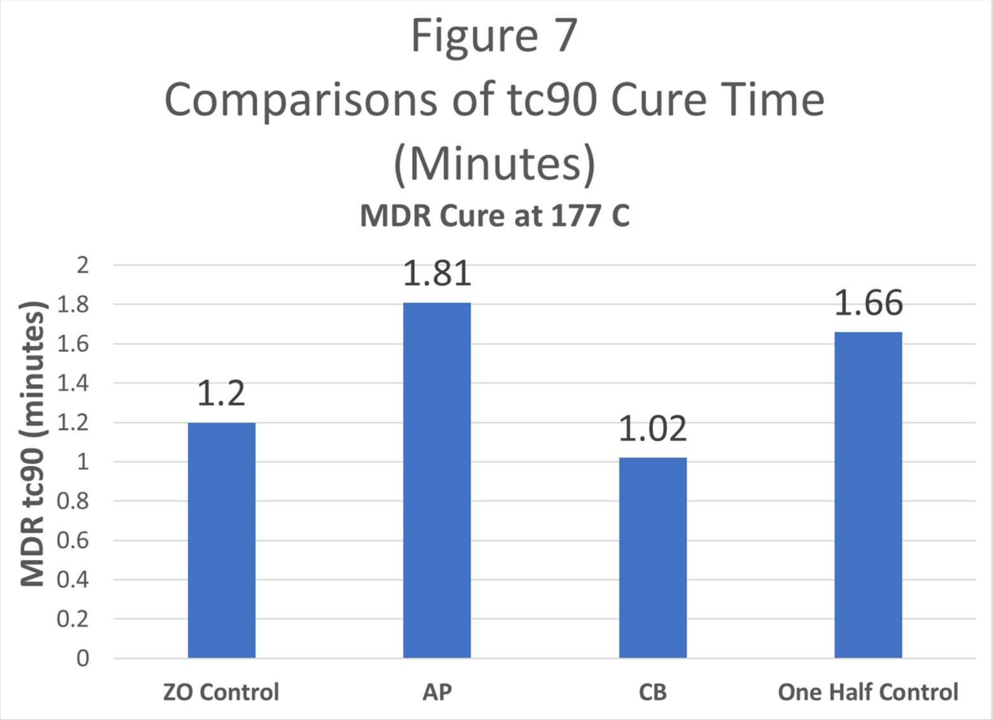
A lab intermesh mixer and two-roll mill were used to mix this new high silica tread compound in six passes.

Discussion of Test Results

Test Results from Comparison of Zinc Oxide Grades in Neoprene

According to ASTM D4620, which is designed to evaluate the quality of zinc oxide in Neoprene (CR or polychloroprene rubber), the shorter the t_C90 (time to 90 % cure) from MDR testing (ASTM D5289), means the better the quality of the zinc oxide.

Figure 7 below shows the differences in tc90 cure time in the ASTM D4620 recipe at a cure temperature of 177°C.



As can be seen, the zinc oxide control and the commercial blend (CB) both imparted shorter tc 90 cure times than the American Process (AP) and the “one-half” control.

It was also found, by using the Dynamic Mechanical Analyzer (DMA), that cured samples with a higher concentration of zinc oxide, had a tighter crosslink density (lower tan δ) when measured at 0, 30, and 60°C as shown in Figures 8, 9, and 10 below.

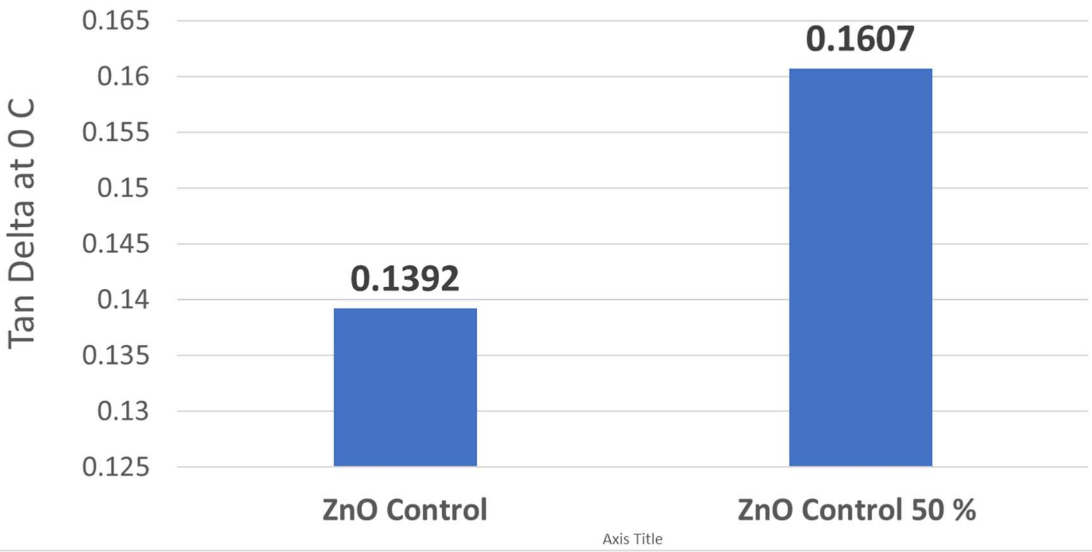


Figure 8

DMA Comparison of tan delta @ 0 C from mixed Neoprene stocks by ASTM D4620

Figure 9

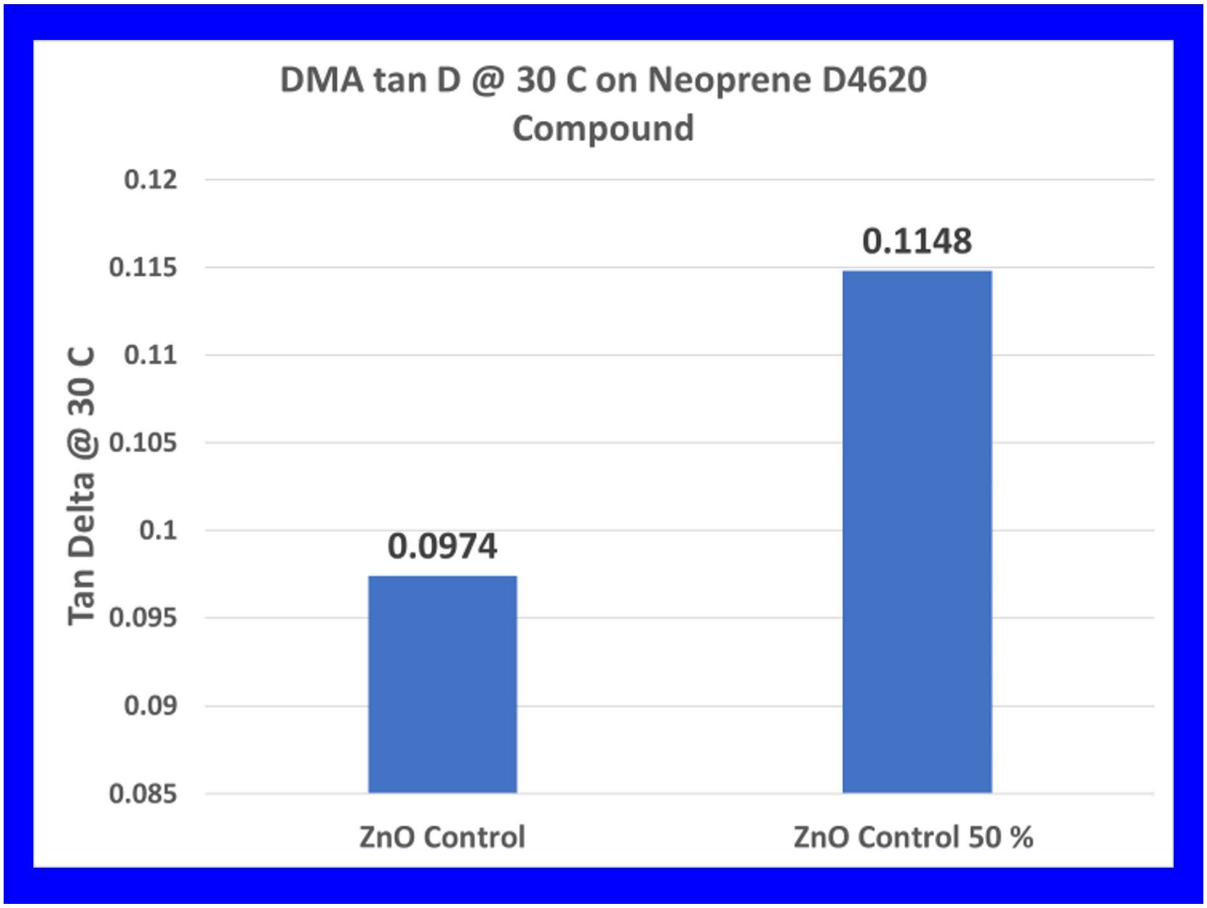
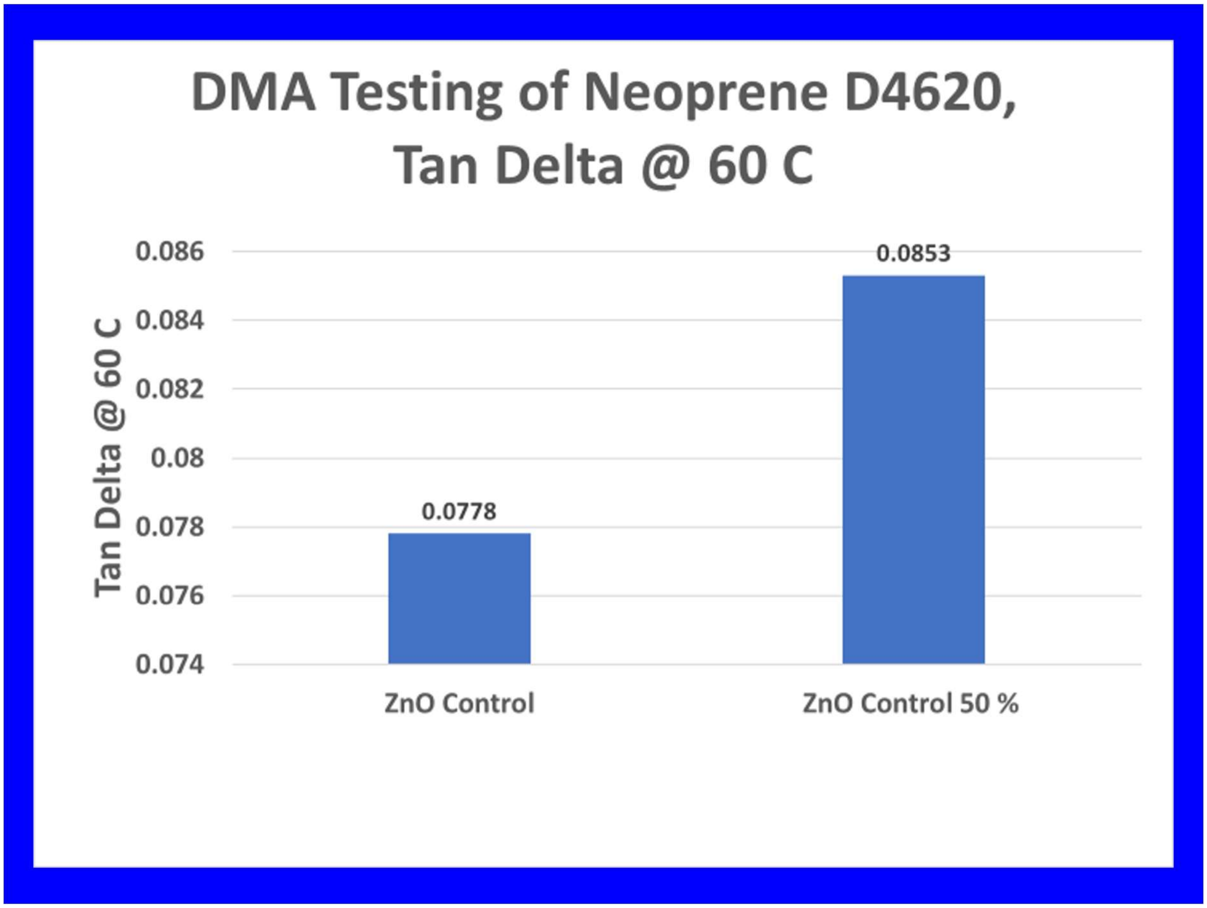

DMA tan D @ 30 C on Neoprene D4620 Compound
Tan Delta @ 30 C
0.12
0.115
0.11
0.105
0.1
0.095
0.09
0.085
0.0974
0.1148
ZnO Control
ZnO Control 50 %

Figure 10



As seen in Figures 8, 9, and 10, the measured DMA tan δ is significantly lower for the ZnO Control vs. the ZnO 50 % control (half the zinc oxide concentration) because the regular control at twice the concentration literates twice the concentration of zinc ions resulting in a much tighter cured crosslink density resulting in the elastic modulus E' rising more from the crosslinks which causes a reduction in the tan δ in that tan δ = E''/E'.

As can be seen, this Neoprene test compound from ASTM D4620 has proven to be effective in judging the quality of a given Zinc Oxide powder used in the industry. However much of the rubber industry, i.e the Tire Industry, does not use neoprene. Therefore, we will discuss the performance of these subject zinc oxide grades in two very critical tire formulation, i.e. the tire wire coat compound and the new highly loaded silica tread (for lower rolling resistance).

Of course, other traditional tests, such as tensile testing, hardness, etc. were also performed on this neoprene formulation but did not have a good enough statistical test sensitivity (signal to noise ratio) compared to the DMA and MDR results.[10,11]

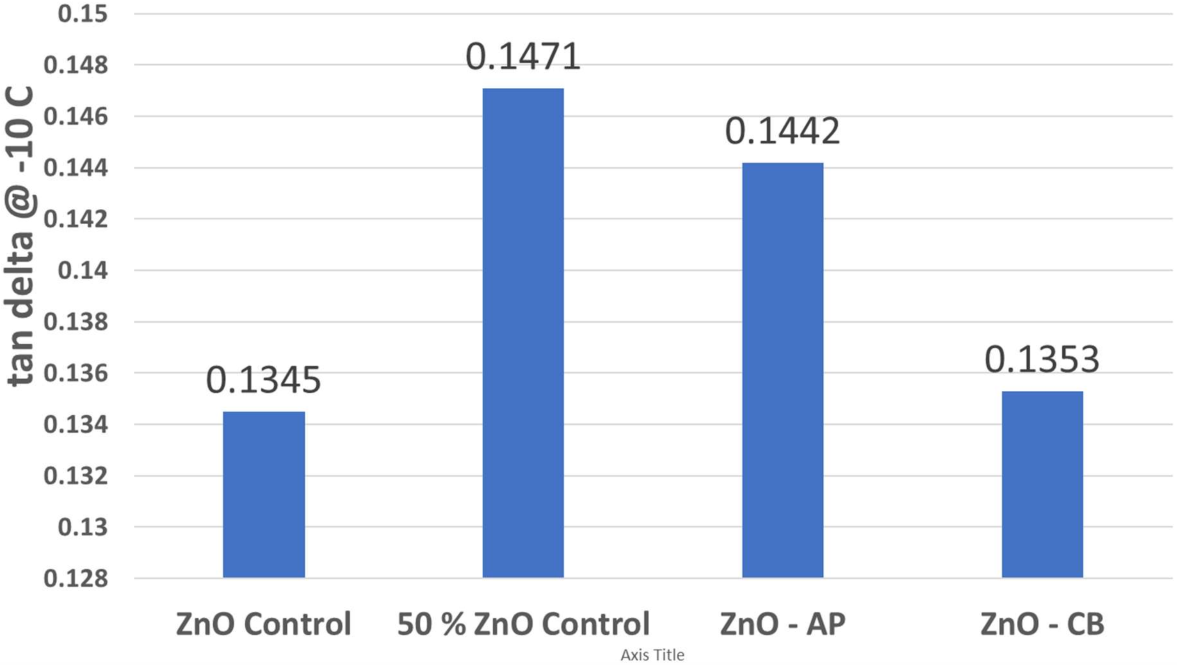
Test Results from Comparison of Zinc Oxide Grades in Tire Belt Skim Coat Compound

As is well known, tire wire coat stock quality is extremely important for steel tire cord adhesion. But sometimes finding quality tests that can repeatedly see zinc oxide quality differences is a challenge. Just as with the Neoprene stock before, DMA testing was again able to detect quality differences among different zinc oxides used in our model tire coat compound.

Figures 11, 12 and 13 show the DMA test results for the wire coat compound.

Figure 11

Comparison of Zinc Oxide Samples in Wire Skim Coat Compound for tan delta @ -10 C



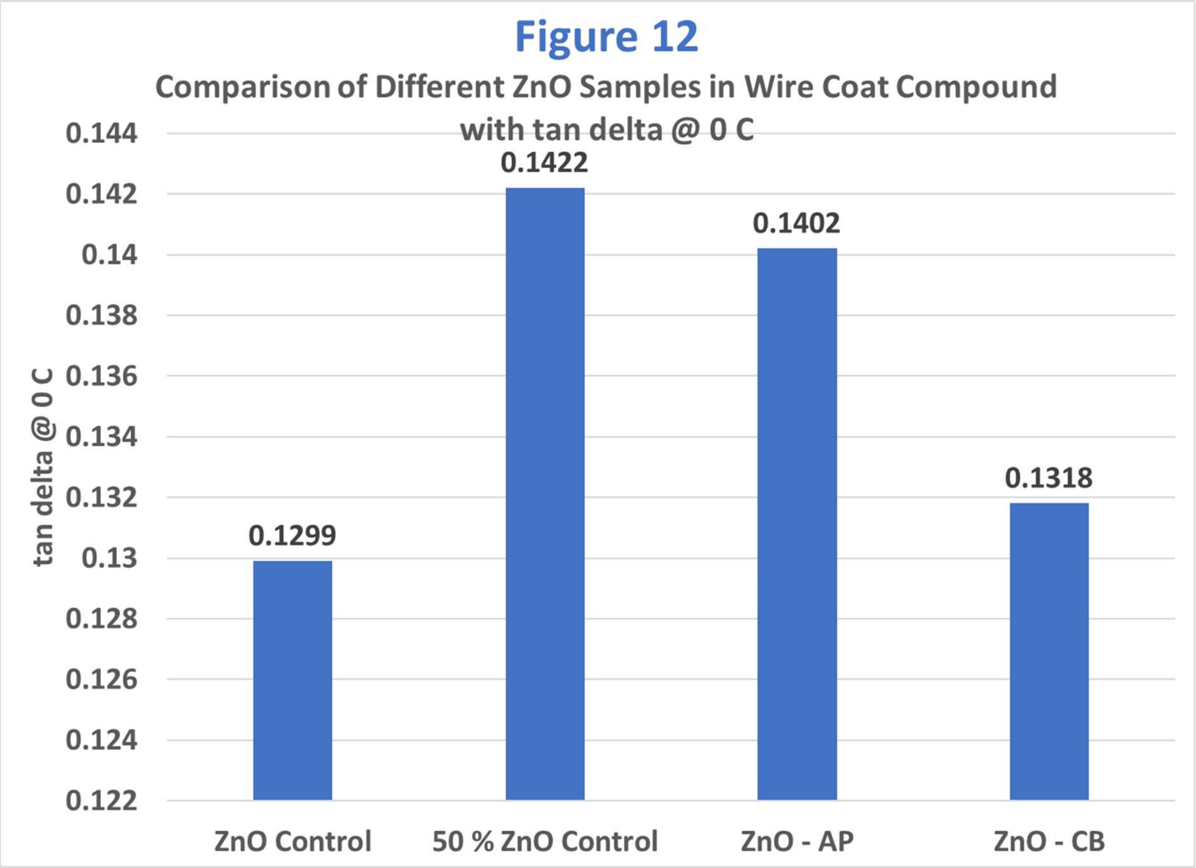
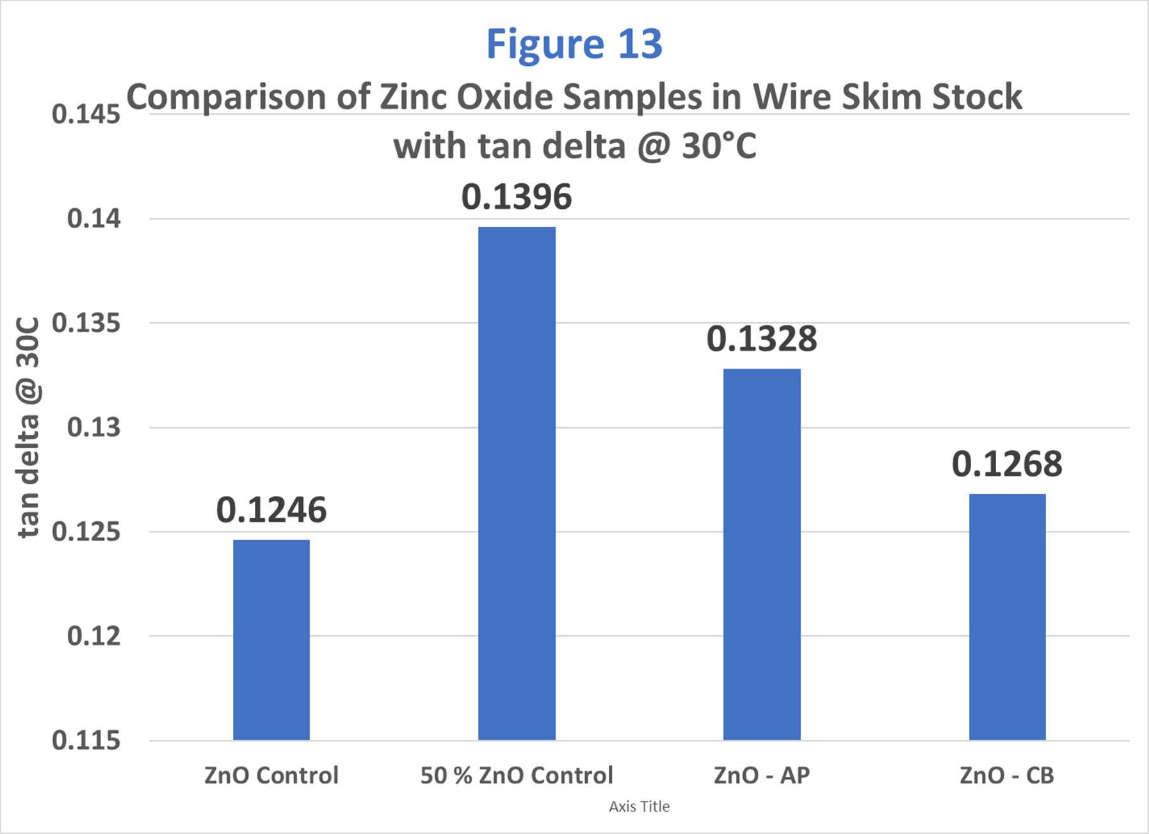


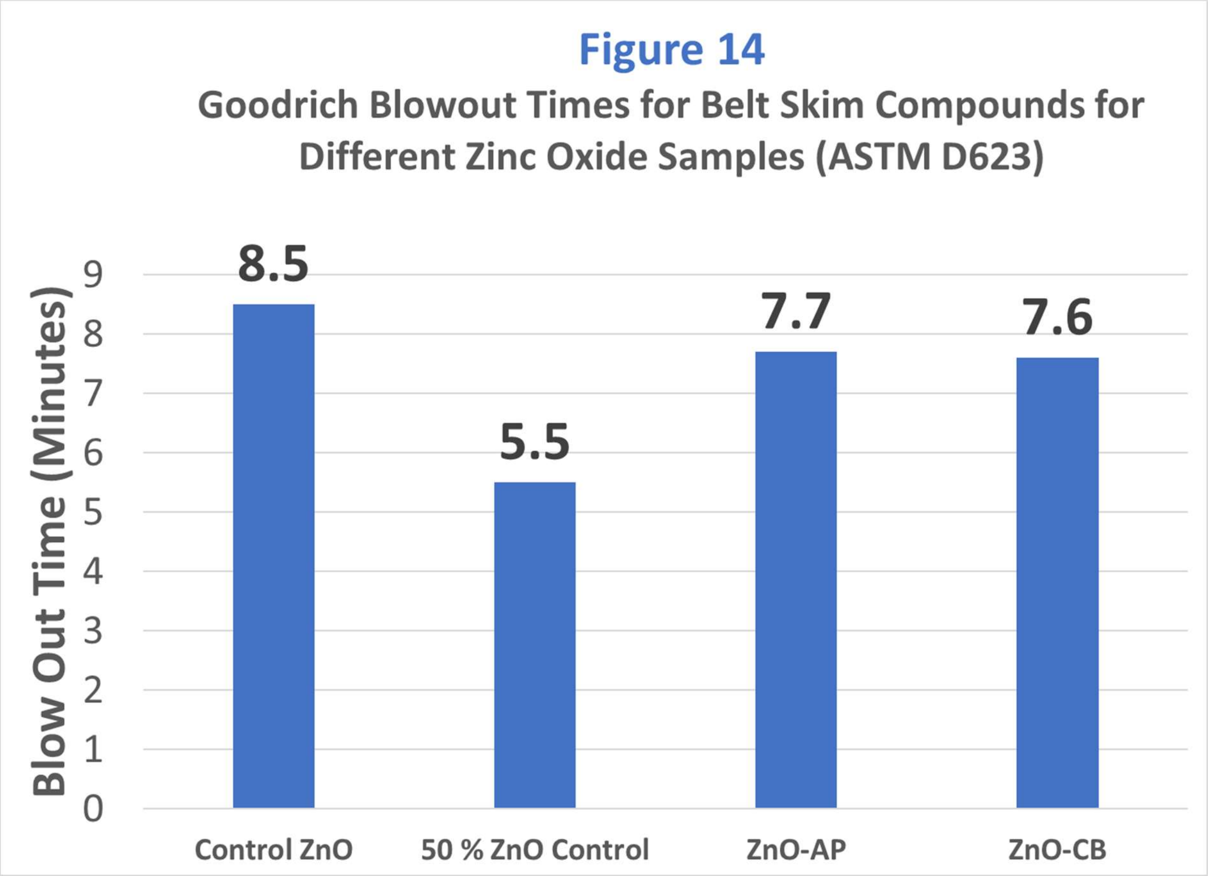
Figure 12

Comparison of Different ZnO Samples in Wire Coat Compound with tan delta @ 0 C



From Figures 11, 12, and 13, one can see that the DMA cured tan δ is quite sensitive to different zinc oxide samples used at 6 phr in the wire coat stock shown in Figure 5. The American Process (AP) and the 50 % ZnO control were both significantly deficient in the amount of zinc ion that they could provide to establish a good crosslinked network which explains why the tan δ values are higher. Also please note that the French Process ZnO (control) has a slightly lower tan δ than the Commercial Blend (CB) zinc oxide indicating that the French Process ZnO gives the tighter (better) crosslinked network.

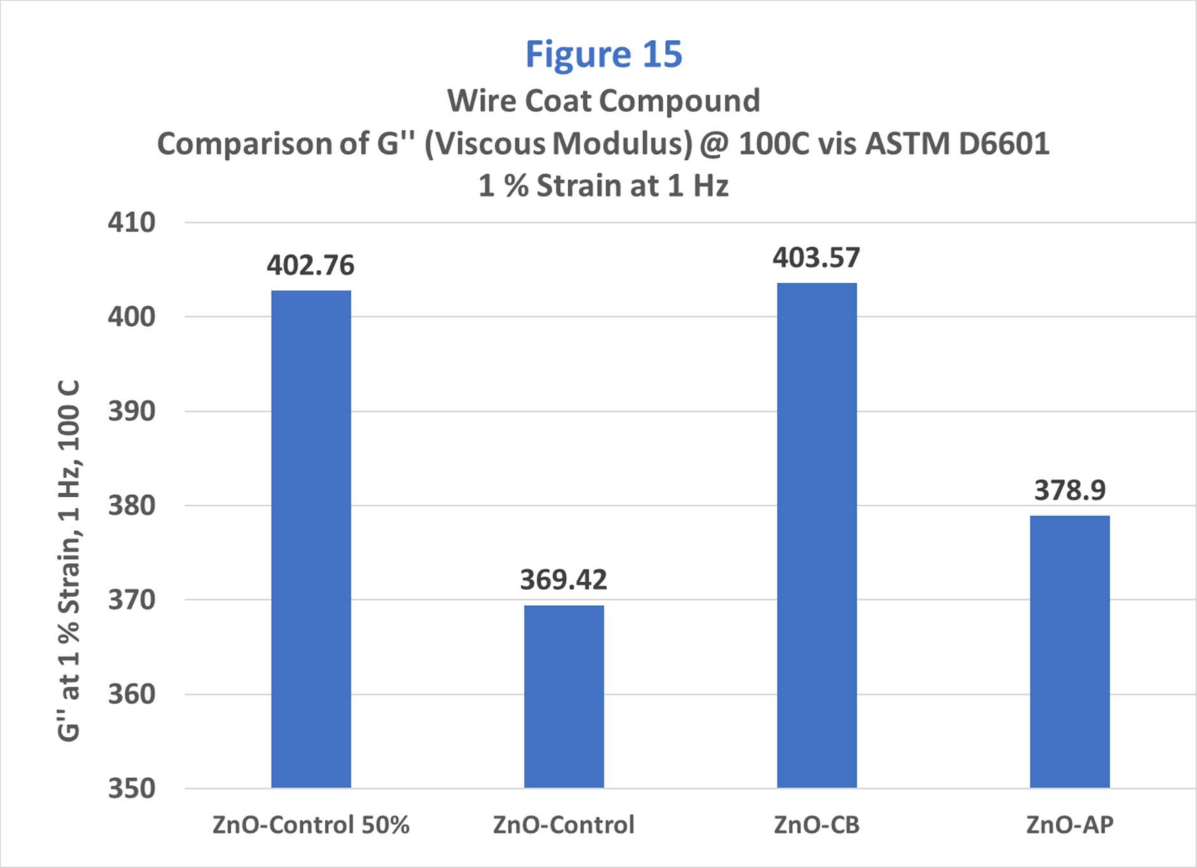
A similar sensitivity to different zinc oxide quality is shown with the Goodrich flexometer test, when run under severe “blow out” conditions[12] with a applied higher stroke of 25 % (ASTM D623) in Figure 14.



As can be seen from the Goodrich Flexometer time-to-blowout data given in Figure 14, the premium French Processed zinc oxide control gave the best (longest) blowout values compared to all the other zinc oxide samples. This data was all collected by running the Goodrich Flexometer to failure (when the cured rubber sample gets so hot internally that gas actually "blows" out the sides of the cylindrical shaped sample. Some people feel that this "blowout" test is much more sensitive to the true quality of the rubber compound than the conventional heat buildup Goodrich Flexometer test that is performed at a less severe stroke (deformation).

Also, the RPA (Rubber Process Analyzer) was also used to evaluate the quality differences among the subject zinc oxide grades used in the wire coat compound evaluation. The RPA was configured to perform ASTM D6601 for curing the subject compounds in place and measuring sinusoidally the after-cure dynamic properties at a lower temperature (100°C)

Figure 15 below compares the after-cure G'' (loss moduli) that is imparted by the four subject zinc oxide samples.



From the RPA data presented here, the higher cured G’’ viscous modulus values may be due to relative deficiencies in the zinc ion concentration causing a deficiency in the density of the crosslinked network. So, in this situation, the lower the G’’ viscous modulus means the better the resiliency of the crosslinked network. So, the “commercial blend” or CB did not do as well as the control (from the French Process).

Figure 16 reinforces what was learned from Figure 15 above. The same relation can be seen at the higher strains.

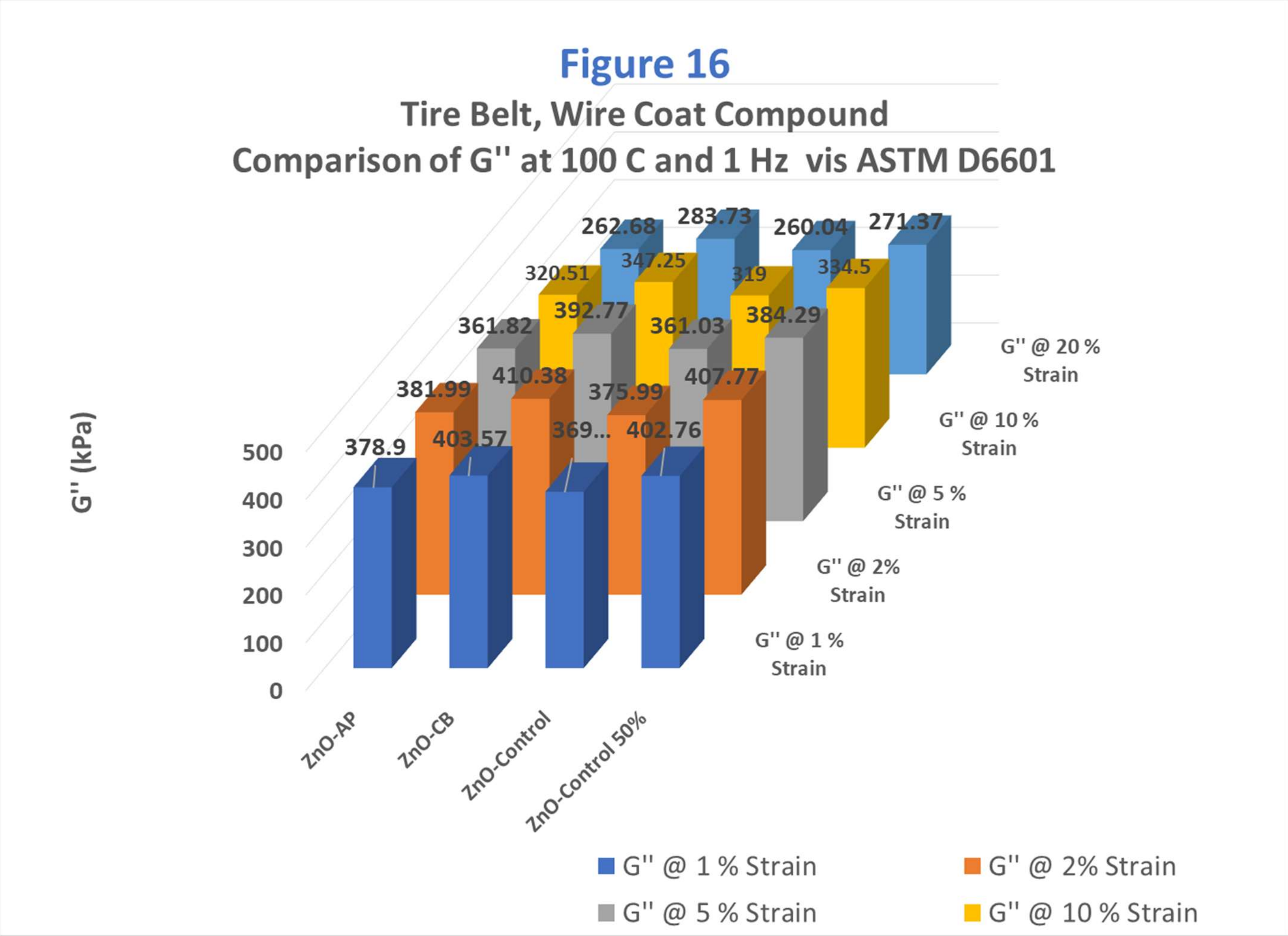
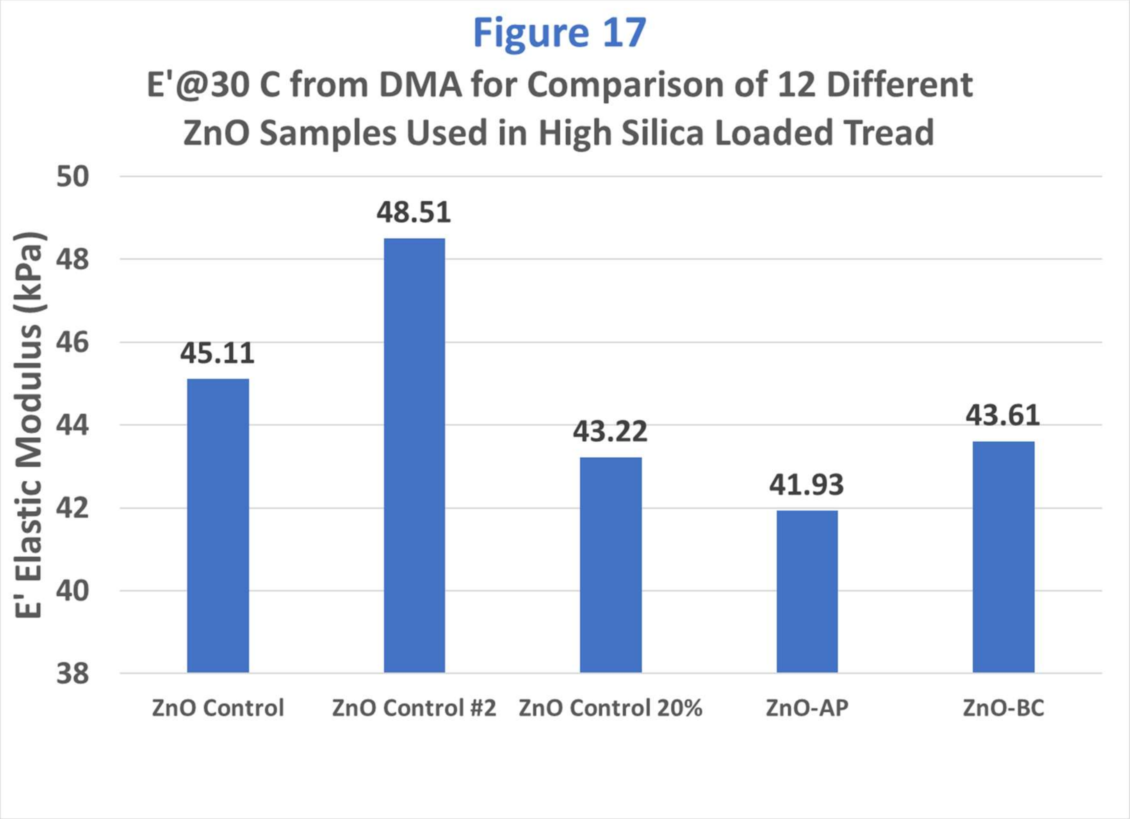


Figure 16
Tire Belt, Wire Coat Compound
Comparison of G'' at 100 C and 1 Hz vis ASTM D6601

Test Results from Comparison of Zinc Oxide Grades in the New 3rd Generation High Silica Tread (at 110 phr Silica)

This special experimental silica tread stock, with 110 phr silica, was very hard to mix and required 6 passes. Therefore, we used two of the same French Zinc Oxide controls (not just one, as we did earlier) to help determine how homogeneous we were in our mixing. So, if the values for each of these two controls disagree significantly, then there is probably significant heterogeneity because of the complexity of mixing this 3rd generation silica tread with 110 phr silica. Also, because this new model recipe only has 1 phr zinc oxide, we decided to change the 50 % Control to a 20% control.

Figure 17 shows the DMA cured elastic modulus E'@30°C for each of the five batches that were mixed for this 3rd generation silica tread stock.



In Figure 17, the cured elastic Modulus E' is reflecting the integrity of the cured elastic crosslinked network that has formed from the vulcanization process. As mentioned earlier, there is some concern regarding the state of dispersion with 110 phr of silica. So, the values for the two French Processed ZnO controls do not agree exactly because of some degree of heterogeneity; however both E' control values are higher than the other E' values for the American Processed (AP) and the Commercial Blend (CB).

ASTM D8059 for measuring the Payne Effect (strain softening) for purposes of measuring state-of-mix before cure was also performed using the RPA. The results of these RPA measurements are shown in Figures 18 and 19 below.

Figure 18

Uncured G' @ 0.070% Strain, 1 Hz, 70 C
ASTM D8059 Payne Effect

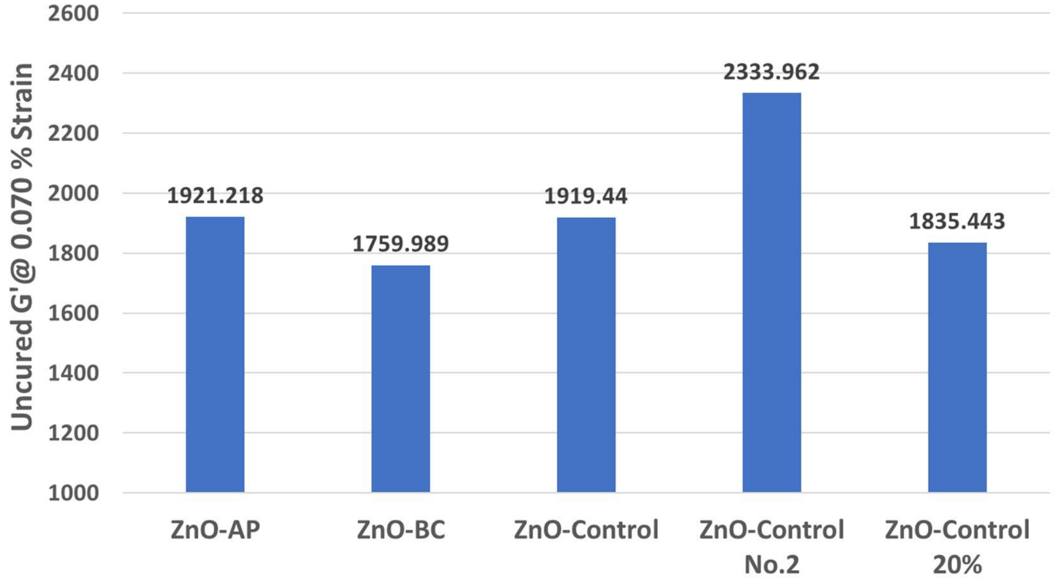
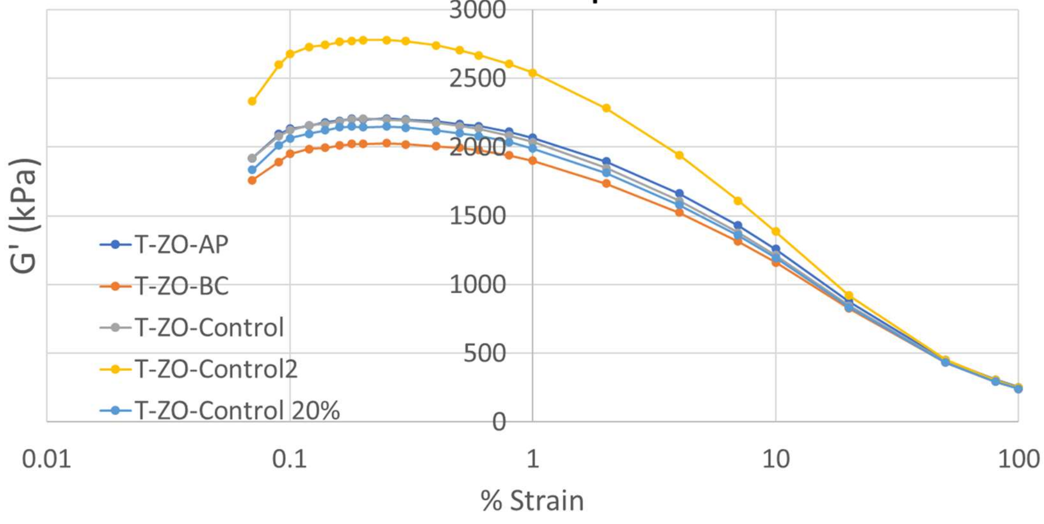


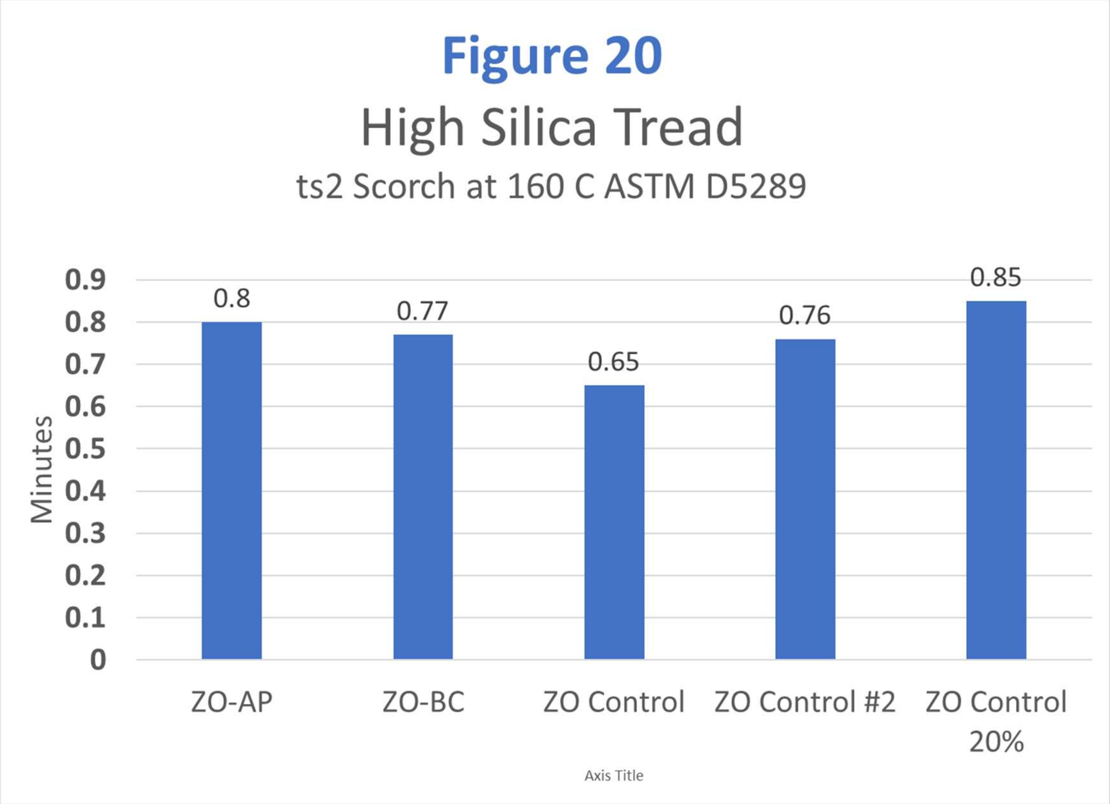
Figure 19

Comparison of the Payne Effect for Five Different ZnO Samples in Low Rolling Resistance, High Silica Tread by ASTM D8059 Strain Sweep



From these figures, it appears possible that the type of zinc oxide that you use for the silica tread might possibly have some effects on the silanization chemistry.

Figure 20 for MDR testing, shows that the French Processed ZnO controls tended to activate the cure a little faster than the American process or the Commercial Blend (CB) as shown below.



Conclusions

1. Overall, the Zinc Oxide Control, from the Indirect “French” Process, outperformed the Zinc Oxide from the Direct “American” process and the typical high volume “Commercial Blend” (CB) zinc oxide that is used today. This was seen with both the tire wire coat compound and the 3rd Generation Silica Tread compound.

2. The Zinc Oxide Control from the “French” Process is compliant with ASTM D4295 for zinc oxide used in rubber.

3. DMA, RPA, MDR, and the Goodrich Flexometer under “blow out” conditions all proved very effective in measuring subtle quality differences seen among different grades of zinc oxide. Statistically it is believed that these tests have a better test sensitivity (signal-to-noise ratio) than many other traditional rubber tests.

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