Highly dispersible silica for improved tire performance

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Executive summary

Precipitated silica is used to improve the in-service performance of passenger car tires. Developing tread compounds with highly dispersible silica (HDS) increases the laboratory predictors of wet traction and rolling resistance while maintaining the wear resistance compared to carbon black-filled compounds.

As a result of the EU regulations mandating the labeling of all tires for rolling resistance, wet traction and noise levels, the use of silica in tire treads is expected to increase. A series of highly dispersible silicas have been developed for use in various tire components, particularly the tread and carcass compounds.

Eecosil-brand silicas are manufactured to different surface areas and all are highly dispersible silicas. The laboratory properties of Eecosil 350MG compounds are compared to N234 carbon black and commercial silicas, including an HDS, in a synthetic rubber tread formulation used as a model for an all-season passenger car tire.

The results of varying the mixing sequence on the cure, cured physical properties, filler dispersion and dynamic properties predictive of winter traction, wet traction, handling and rolling resistance are presented.

As a result of the Common Position (EC) No. 18/2009 adopted by the European Parliament and the Counsel for the European Union in November 2009, the labeling of tires with respect to fuel efficiency and other essential parameters became mandatory Nov. 1, 2012[1] (**Fig. 1**).

The Working Party on Noise, WP.29, developed a one-condition rolling resistance test adopted as ISO 28580 for passenger car (C1), light truck (C2), and truck and bus (C3) tires in order to determine the fuel efficiency class using the rolling resistance coefficient (RRC, kg/t).

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Rauline[2] described an all-season, high-performance passenger tire having silica-filled treads. Specifically, by using a solution-polymerized styrene-butadiene rubber having a high vinyl content, a high cis-butadiene rubber, a highly dispersible precipitated silica[3-4] and a silane coupling agent (**Table I**), the wet traction, snow traction and rolling resistance properties were improved, while maintaining the wear life compared to that of the carbon black-filled tread (**Table II**).

Fig. 1. EU tire label.[1]

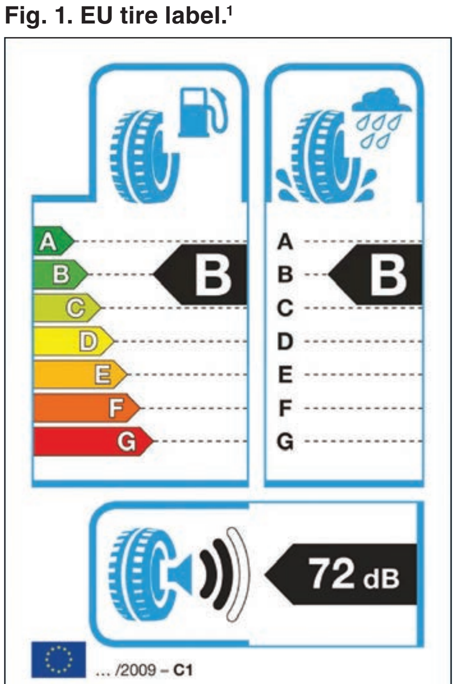

Table 1. Control and silica-filled tread formulations.[2]

Ingredient, phr	T	C	S	N	I
SBR, emulsion	100	100	100		
SBR, solution				75	75
BR, high-cis				25	25
Carbon Black, N234	80			80	
Silica, conventional		80			
Silica, highly dispersable			80		80
Silane Coupling Agent		12.8	12.8		12.8
Aromatic Oil	37.5	37.5	37.5	32.5	32.5
Zinc Oxide	2.5	2.5	2.5	2.5	2.5
Stearic Acid	1	1	1	1	1
Antioxidant	2	2	2	2	2
Paraffin Wax	1.5	1.5	1.5	1.5	1.5
Sulfur	1.35	1.4	1.4	1.35	1.4
Accelerator, Sulfenamide	1.35	1.7	1.7	1.35	1.7
Accelerator, Diphenylguanidine		2	2		2

Table 2. Control and silica-filled tread properties.[2]

	T	C	S	N	I
Transverse adherence on wet ground	100	105	106	101	106
Adherence on wet ground	100	103	104	99	103
Adherence on snow-covered ground	100	104	104	100	104
Rolling resistance	100	113	114	101	115
Travel noise	100	-1 dB	-1 dB	100	-1 dB
Wear life	100	75	85	94	102

The improvements in tire performance are directly related to the amount of precipitated silica present, with the best results obtained without the use of carbon black.[2] Highly dispersible precipitated silicas have been characterized as those which break easier upon ultrasonic treatment of a water/silica dispersion, leading to a lower number of particles with diameters greater than 50 µm (D50),[4] or those which upon mixing in rubber break up to form smaller particles called agglomerates as determined by optical microscopy.[5-7]

We use a similar silica-filled all-season passenger car tire tread formulation as a model in order to evaluate the compound properties of Eecosil-brand 350MG, and compare to the performance of a N234 carbon black-filled control and to two silica-filled tread compounds using a semi-dispersible silica and a highly dispersible silica (HDS).

Experimental

All experiments were performed at the Akron Rubber Development Laboratory in Akron, Ohio. Eecosil 350MG (CTAB surface area[8] and nitrogen surface area[9] ~ 160 m^2/g) was provided to ARDL. All other materials were purchased by ARDL and used as received. The tread formulations are shown in **Table III**.

Because a laboratory internal mixer equipped with intermeshing rotors was not available, compounds were mixed on a laboratory-scale Banbury-brand internal mixer using a 3-pass, a 4-pass and a 5-pass mixing sequence. Tread compounds were compared in order to determine the ease of dispersion of the three silicas to one another, and to the N234 carbon black control compound and the effect upon physical and dynamic properties.

In all sequences, the Stage 1 mix is to masticate the elastomers, incorporate and disperse the fillers, add the processing oil and performance aid, and increase the rotor speed to achieve and maintain a temperature that allows for the hydrophobation reaction of the organosilane with the silanol (Si-OH) groups on the silica surface.[10-11]

For the 3-pass mix, a Stage 2 non-productive mix adds the TMQ antioxidant, DPG accelerator and ZnO cure activator to the Stage 1 masterbatch in a simple a 3-minute mix. Stage 3 is the finalization step adding the remaining curatives to the Stage 2 masterbatch in a 2.5-minute mix, but maintaining the temperature <105°C by reducing the rotor speed.

The 4-pass mix introduces a 3-minute remix step as Stage 3 prior to the finalization step. The 5-pass mix introduces a remix of the Stage 1 masterbatch as Stage 2 prior to the Stage 3 non-productive mix where the TMQ, DPG and ZnO are added. Stage 4 is a second 3-minute remix of the Stage 3 masterbatch without the addition of ingredients, and Stage 5 is the finalization step. **Table IV** is a summary.

Physical properties were tested according to standard protocols. Moving die rheometer was measured according to ASTM D5289 @160°C. Specimens were cured for a time corresponding to T90 + 5 minutes @160°C for Shore A hardness and tensile properties (ASTM D412-98a using a type die C dumbell).

Angle abrasion was measured according to ISO 23233 using a 6° blade angle and using an alternating 2° and 6° blade angle.

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Table 3. Model N234 control and silica-filled tread formulations.

Ingredients	Trade Name	phr	phr
S-SBR	Duradene 738	75	75
BR	Budene 1207	25	25
Carbon Black	N234	80	5
Silica	Eecosil 350MG		75
Silane	SCA985		6
TDAE Process Oil	Vivatec 500	30	10
Performance Aid	Escorez 5600		20
Accelerator	DPG	1.5	1.5
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
	Total	215.75	221.75

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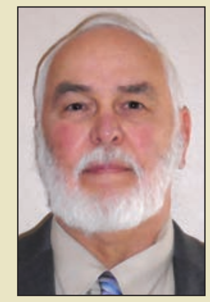

Evans

Waddell

Walter Waddell currently is the senior technology coordinator for both Cheng Shin Rubber Industries Co. and Oriental Silicas Corp. He also is co-chair of the International Tire Exhibition and Conference.

He previously had retired from ExxonMobil Chemical as a senior research associate. Prior to that he had been a section head at Goodyear and a senior scientist for PPG.

Waddell received his bachelor's in chemistry from the University of Illinois at Chicago and his doctorate in chemistry from the University of Houston. He also was a research associate at Columbia University and an associate professor at Carnegie-Mellon University.

Waddell has 37 patents, five trade secrets, 153 publications, and 162 presentations. He is a member of the American Chemical Society; the ACS Rubber Division, for which he was chairman in 2011; and ASTM International committees D-11 (Rubber) and F09 (Tires).

His awards include: Distinguished Corporate Inventor; Award of Appreciation, ASTM F09; ACS Rubber Division Sparks-Thomas Award, Melvin Mooney Distinguished Technology Award, Distinguished Service Award and Outstanding Service Award; International Rubber Conference Medal; ACS Greater Houston Section Joe Hightower Award; and ACS Southeast Regional Award.

Larry Evans retired from the Transportation Research Center as a research analyst assigned to the National Highway Traffic and Safety Administration.

His primary responsibility was to analyze data from NHTSA's extensive tire and vehicle testing programs.

He has had a varied background in the tire industry, beginning with Goodyear, where as a research chemist he worked on rubber compounding and fabric to rubber adhesion for tires and for industrial engineered products.

Evans was a senior research associate at PPG, and then technology manager at J.M. Huber responsible for global research and implementation of silica for the rubber, plastics, and coatings industries.

Evans has 12 patents, authored 60 scientific publications, and has presented more than 70 technical seminars around the world.

He is a member of the ACS Rubber Division, where he chaired the Program Planning and the Best Paper committees. Evans also is a member of ASTM F09 Committee on Tires, and also the Society of Automotive Engineering.

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Scanning electron micrographs (SEM) were obtained for six fresh cut surfaces, with each view having a minimum resolution of 0.2 microns. Micrographs were analyzed using ImageJ software,[12] a Java program, in order to determine the percent-white areas representing the undispersed filler agglomerates.

The distribution of the undispersed white particles also was determined as a function of agglomerate size. Dynamic properties were obtained using a Metravib DMA150 Dynamic Mechanical Analyzer. Temperature sweeps with a 1°C/minute cooling rate from 70°C to -30°C were used at 10Hz and 2 percent dynamic strain.

Results and discussion

Cure. Cure properties change on going from a 3-pass => 4-pass => 5-pass mix. ML, MH and delta torque (MH-ML) decrease with increasing mixing; for example see delta torque in **Fig. 2** (R2 varies from ~0.9 to 0.997).

Cure times (TS2 scorch, T50 and T90) of silica-filled treads are significantly longer than the N234 compound, but do not show a statistically significant trend with increasing mixing; for example see T90 in **Fig. 3**.

Cure curves of compounds prepared using the 5-pass mixing sequence are shown in **Fig. 4**.

Physical Properties. Hardness values generally decrease with increasing mixing. Tensile strength and elongation @ break values do not show a statistically significant trend. The 50 percent modulus (M50) and 100 percent modulus (M100) values decrease (see **Figs. 5 and 6**), and the 300 percent modulus (M300) values increase with increasing mixing, (see **Fig. 7**.)

N234 and Eecosil 350MG show linear changes with R2 > 0.9. The semi-dispersible silica showed the lowest correlations.

The M300/M100 ratio, also called the reinforcing index13-20, and the M300/M50 ratio[21] have been used as indicators of the effectiveness of the hydrophobation chemical reaction of the organosilane with the silanol (Si-OH) groups on the silica surface. The change (+3 percent) for the M300/M100 ratio of N234 compounds from the 3-pass to a 5-pass mix, indicates better carbon black dispersion.

The M300/M100 changes for the three

Table 4. Summary of 3-pass, 4-pass and 5-pass mixing sequences.

Mix Stage	3-Pass Mix	4-Pass Mix	5-Pass Mix
One	Add polymer, fillers, oil and resin		
Two	Add other ingredients		Remill
Three	Add curatives	Remill	Add other ingredients
Four		Add curatives	Remill
Five			Add curatives

Fig. 2. MH-ML Delta torques for N234-control and silica-filled treads, with R2=0.993, 0.978, 0.899 and 0.997, respectively.

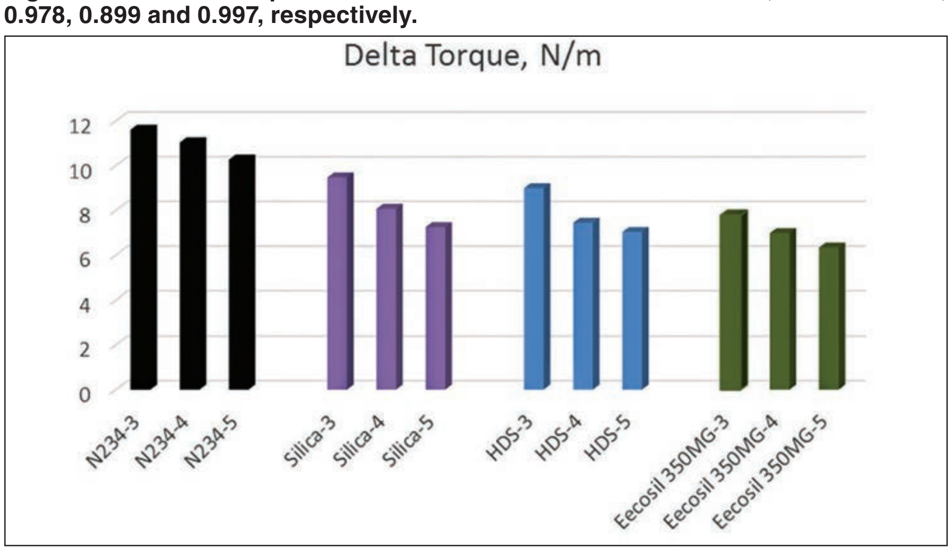


Fig. 3. T90 Cure times for N234-control and silica-filled treads.

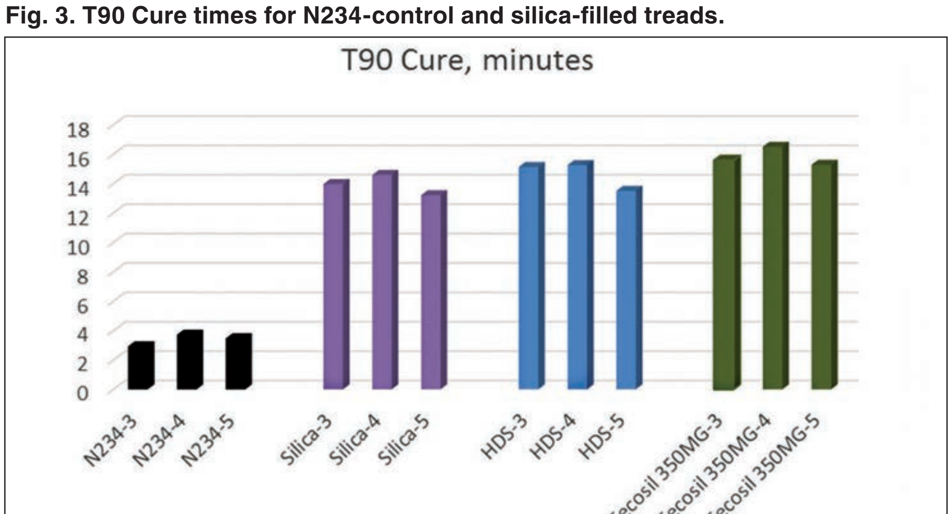


Fig. 4. Cure curves for N234-control and silica-filled treads.

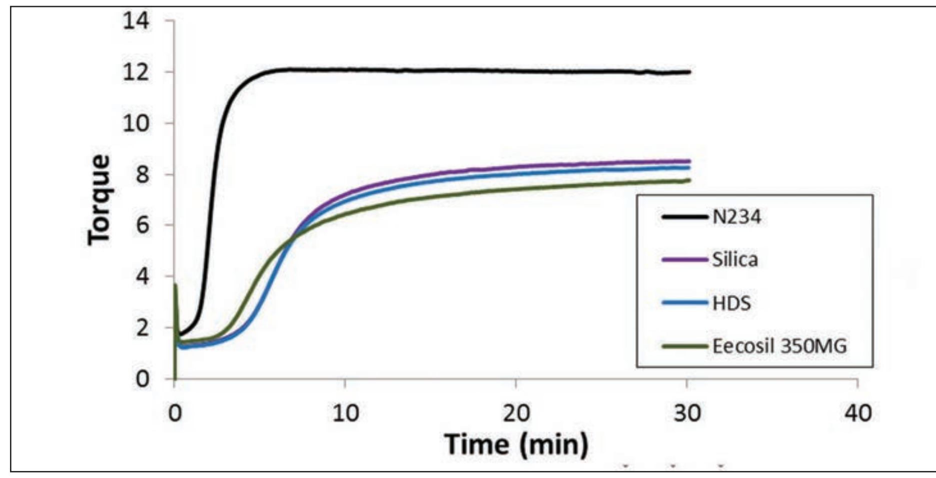


Fig. 5. 50 percent modulus values for N234-control and silica-filled treads, with R^2=0.958, 0.113, 0.709 and 0.945, respectively.

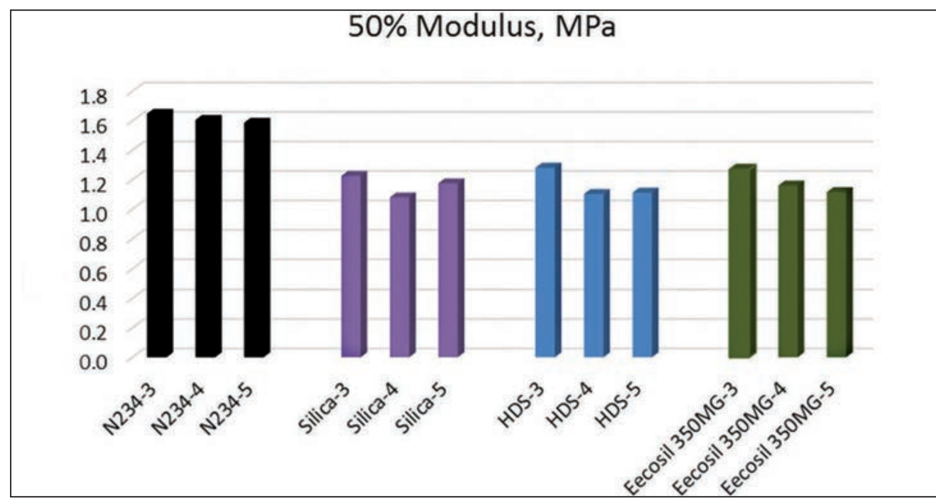


Fig. 6. 100 percent modulus for N234-control and silica-filled treads with R^2=0.912, 0.001, 0.599 and 0.909, respectively.

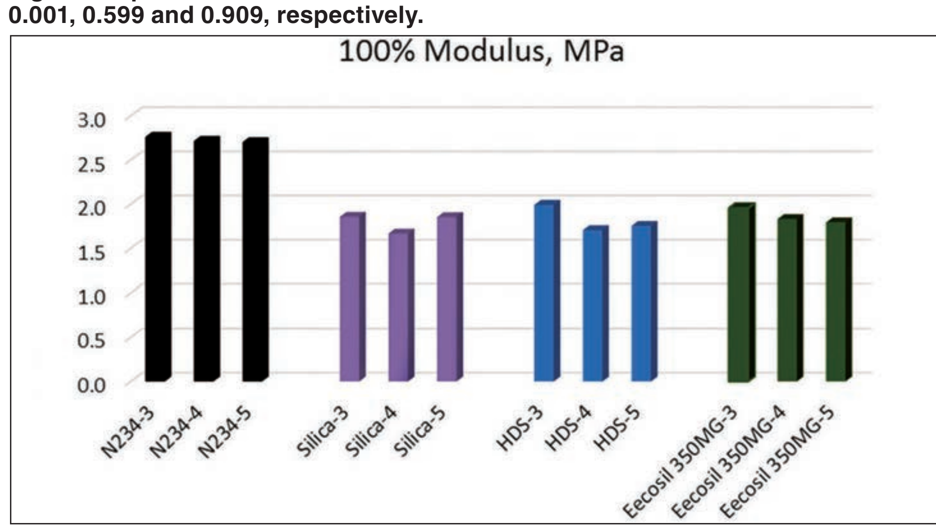
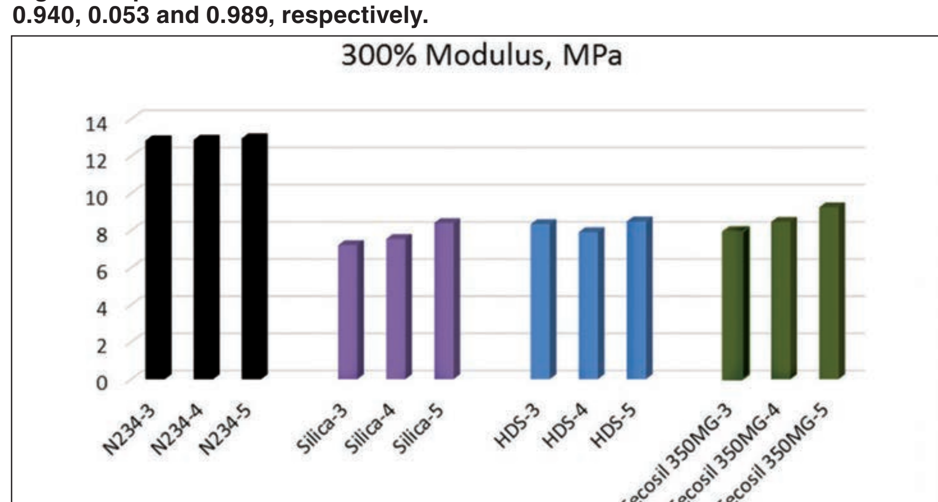


Fig. 7. 300 percent modulus for N234-control and silica-filled treads with R^2=0.948, 0.940, 0.053 and 0.989, respectively.



silica-filled treads are much higher. The Eecosil 350MG compounds show the largest increase (+27 percent) from the 3-pass mix to a 5-pass mix (**Fig. 8**), which probably indicates not only the better filler dispersion but also the most efficient hydrophobation chemical reaction of the organosilane with the silica silanols, and subsequent coupling to the polymer matrix during curing.

The change (+5 percent) for the M300/M50 ratio of N234 compounds from the 3-pass to a 5-pass mix, indicates better carbon black dispersion. Again, the M300/M50 changes for the three silica-filled treads are much higher.

The Eecosil 350MG compound also shows the largest increase (+33 percent) from the 3-pass mix to a 5-pass mix (**Fig. 9**), which indicates not only the best dispersion but also the most efficient hydrophobation chemical reaction of the organosilane with the silica silanols.

Abrasion Resistance. The blade abrasion index for the three silica tread compounds shows no statistically significant trend with increasing mixing from the 3-pass to the 5-pass mix, but does show that the HDS and the Eecosil 350MG silicas have higher values than the semi-dispersible silica compound using the 5-pass mixing sequence. See for example **Fig. 10** showing the abrasion index using an alternating blade angle of 2° and 6°. Similar results are obtained using only a 6° blade angle.

Filler Dispersion. Scanning electron micrographs for the 3-pass, 4-pass, and 5-pass mixes show that the N234 carbon black control and the Eecosil 350MG compounds have the best dispersions based upon the visible white areas. The semi-dispersible silica compound shows the poorest dispersion **(see Fig. 11)**.

The percent-white areas of micrographs were obtained by integration. Averaging the areas of all six micrographs obtained for each mixing sequence for each of the N234 and three silica compounds, gives the percent-white areas shown in **Fig. 12**.

Thus, by using a 5-pass mixing sequence, silica compounds can be dispersed on a laboratory Banbury internal mixer. Particle size distributions were determined **(Fig. 13)** with the semi-dispersible silica having the highest numbers and N234 black and Eecosil 350MG giving the lowest numbers of large agglomerates **(Fig. 14)**. Thus, Eecosil 350MG is a highly dispersible silica **(Fig. 15)**.

Dynamic Properties. Temperature-dependent tangent delta curves show the expected result that compared to the N234 carbon black control, all three silica-filled tread compounds give lower predicted rolling resistance based on tangent delta @60°C values and higher predicted wet traction based on tangent delta @0°C values **(Fig. 16)**.

Tangent delta values are dependent upon the mixing, decreasing values with increased number of mixing steps; for example see **Fig. 17,** which shows selected results for 3-pass and 5-pass mixes. G' values follow the same trend **(Fig. 18)**.

Summary

Using a Banbury mixer to disperse highly filled silica tread compounds can be accomplished by using a 5-pass mixing sequence, instead of using an internal mixer with intermeshing rotors.

Cure and physical properties differ for the compounds prepared using a 3-pass, a 4-pass and a 5-pass mixing sequence. The most notable change is in the ratio of the 300 percent modulus / 100 percent modulus and the 300 percent modu-

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Fig. 11. SEM micrographs of N234, silica, HDS and Eecosil 350MG tread compounds prepared using a 5-pass mixing sequence.

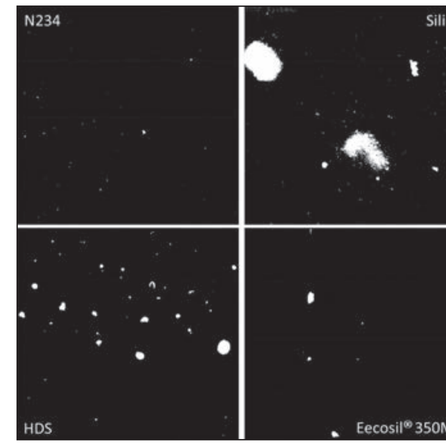


Fig. 8. M300/M100 Ratios for N234-control and Silica-filled treads.

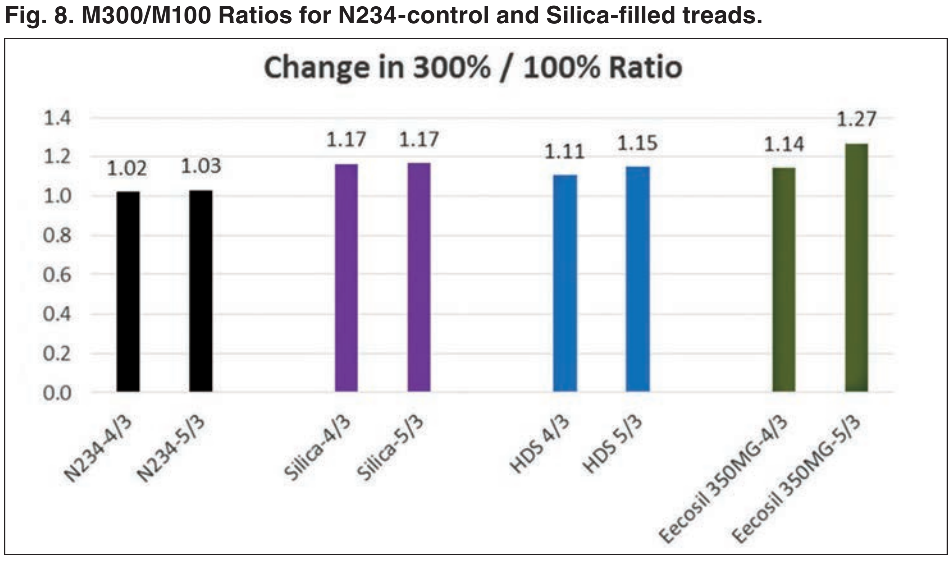


Fig. 9. M300/M50 ratios for N234-control and silica-filled treads.

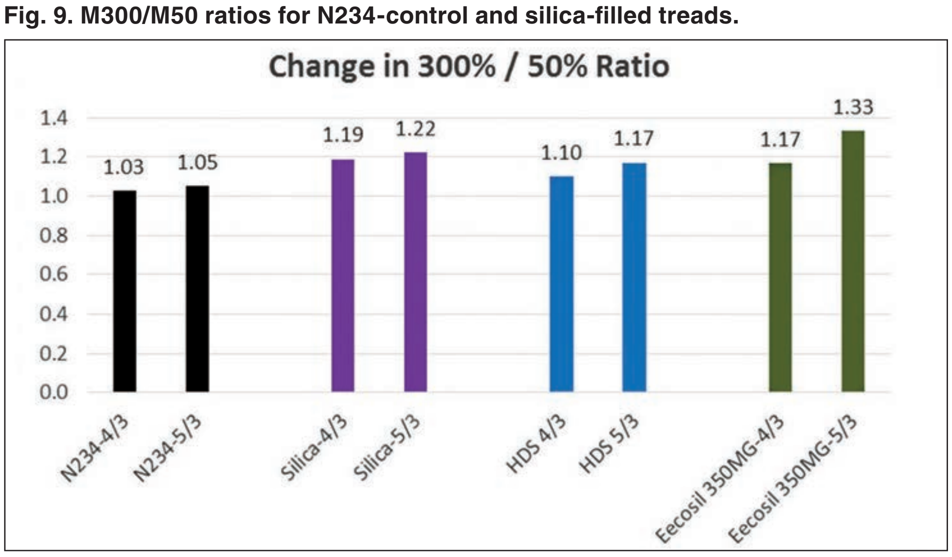


Fig. 10. Blade abrasion Index for silica-filled compounds.

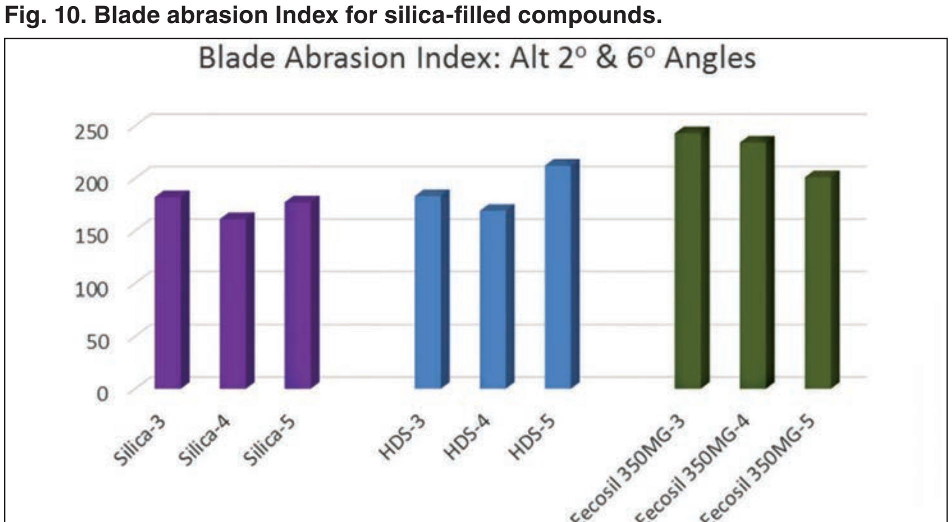


Fig. 12. Graph of the percent-white areas of the SEM photographs.

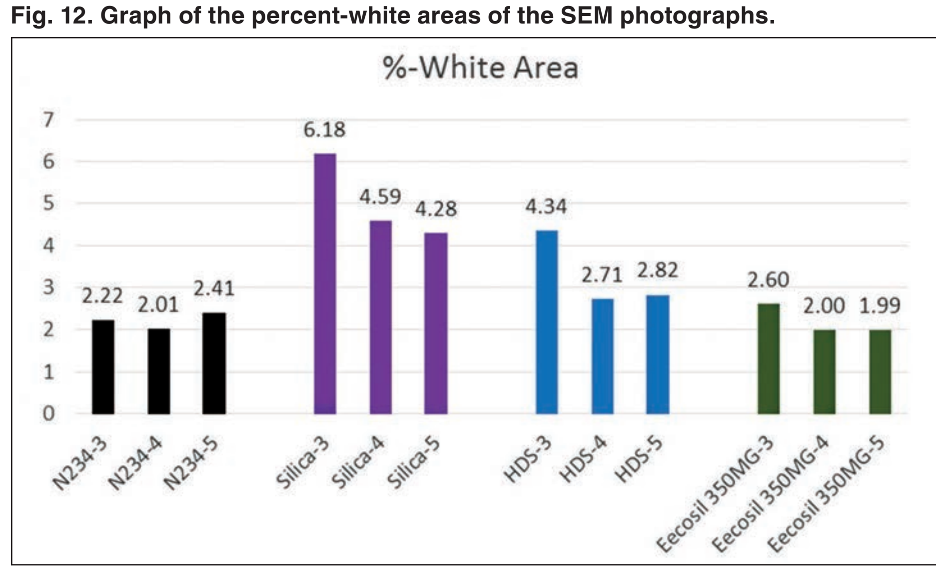


Fig. 13. Distribution of agglomerates into particle size.

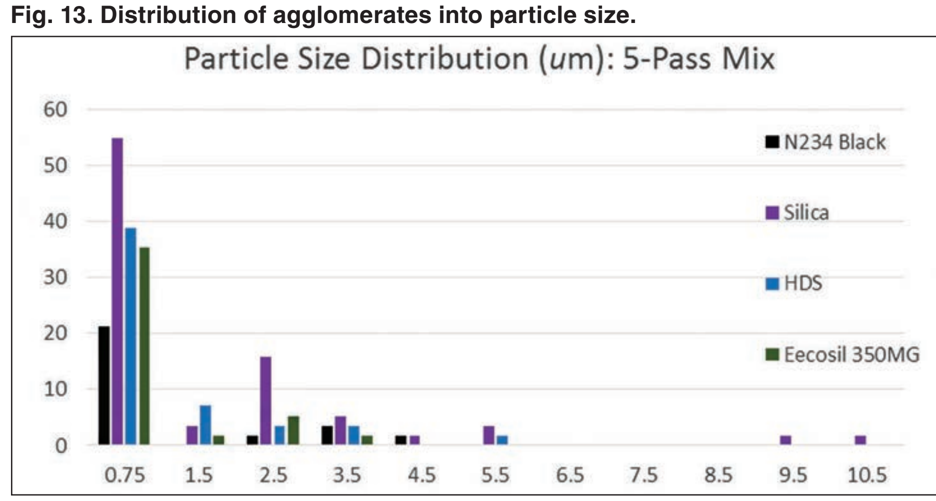
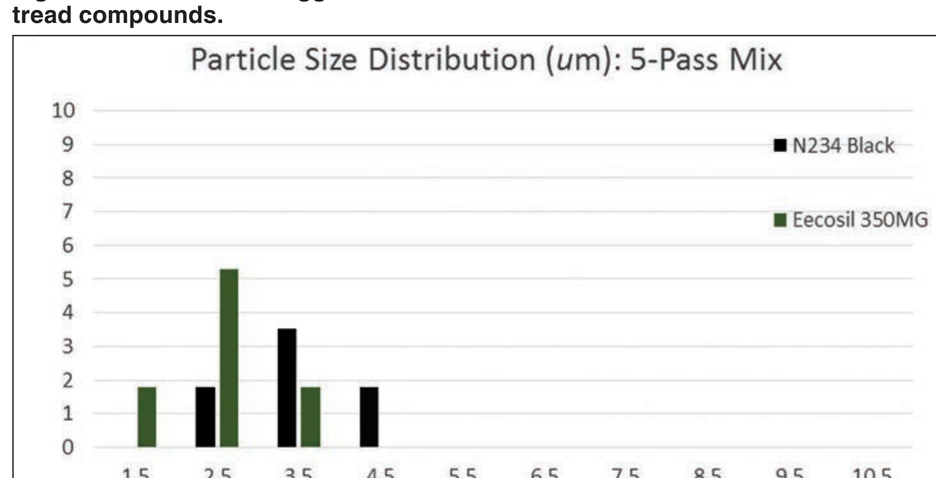


Fig. 14. Distribution of agglomerates for N234 control and Eecosil-brand 350MG tread compounds.



Silica

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lus/50-percent modulus values.

For N234 carbon black, the small 3-5 percent increase is thought to result only from better dispersion. For the silica-filled compounds, better dispersion along with the increased efficiency of the chemical hydrophobation reaction with organosilane increases the M300/M100 and M300/M50 ratios with increasing number of mixing steps.

The semi-dispersible silica does not have as high a ratio or abrasion index values as do the two highly dispersible silicas. The dispersion based on the percent-white area of Eecosil 350MG is the same after the 4-pass and 5-pass mixes; however, the M300/M100 and M300/M50 ratios increase significantly, indicating the higher efficiency of the hydrophobation reaction.

Silica-filled tread compounds give lower tangent delta @60°C and higher tangent delta @0°C values than does the N234 carbon black control, predictive of lower tire rolling resistance and increased wet traction. The balance of dispersion, and important physical and dynamic properties are shown in **Figs. 19 and 20**.

Thus, Eecosil 350MG is a highly dispersible silica.

References

1. Official Journal of the European Union, C 298 E, Vol. 52, 8 December 2009.
2. R. Rauline to Michelin, US 5,227,425 (7/13/93).
3. F. Bomo, Y. Chevallier, P. Lamy and J.-C. Morawski to Rhone Poulenc, U.S. 5,089,554 (2/18/92).
4. P. Cochet, P. Barruel, L. Barriquand, J. Grobert, Y. Bomal and E. Prat (Rhone Poulenc), Rubber World, 210, 20 (1994).
5. W.H. Waddell, P.A. Beauregard and L.R. Evans (PPG), Tire Technol. Int. 1995, 14 (1995).
6. L.R. Evans, J.T. Dew, L.T. Hope, T.G. Krivak and W.H. Waddell (PPG), *Rubber & Plastics News*, July 31, 1995, p. 12.
7. L.R. Evans and W.H. Waddell (PPG), Kautsch. Gummi Kunstst., 48, 718 (1995).
8. ASTM D6845-12, Standard Test Method for Silica, Precipitated, Hydrated—CTAB (Cetyltrimethylammonium Bromide) Surface Area.
9. ASTM D5604-96(2012), Standard Test Methods for Precipitated Silica—Surface Area by Single Point B.E.T. Nitrogen Adsorption.
10. T.A. Okel (PPG), Paper C, Rubber Division, ACS, May 2005.
11. O. Klockmann, and A. Hasse (Degussa), Paper H, Rubber Division, ACS, May 2005.
12. https://rsb.info.nih.gov/nih-image/about.html
13. Y. Chevallier and M. Rabeyrin to Rhone-Poulenc, U.S. 5,403,570, April 4, 1995.
14. W.C. Fultz and L.R. Evans (Huber), Rubber World, April 1998, p 39-43.
15. S.D. Patkar, J.E. Bice, and T.A. Okel (PPG), Rubber World, June 1998, p 21-28.
16. A. Hasse, O. Klockmann, A. Wehmeier, and H.-D. Luginsland (Degussa), Tire Technol. Int. 2000, p 52-59.
17. H.-D. Luginsland and A. Hesse (Degussa), Paper 34, Rubber Division, ACS, Dallas, April 2000.
18. H.-D. Luginsland, J. Frohlich, and A. Wehmeier (Degussa), Rubber Chem. Technol., 75, 563 (2002)
19. J. Vander Kooi (Struktol), Rubber World, April 2005, p 21-23 and 33.
20. C. Hartshorn (Momentive Performance Materials), Tire Technol. Int. 2007, p 74-77.
21. A. Hasse, O. Klockmann, A. Wehmeier, and H.-D. Luginsland (Degussa), Paper 91, Rubber Division, ACS, October 2001.

Fig. 15. Distribution of agglomerates for highly dispersible silica (HDS) and Eecosil 350MG tread compounds.

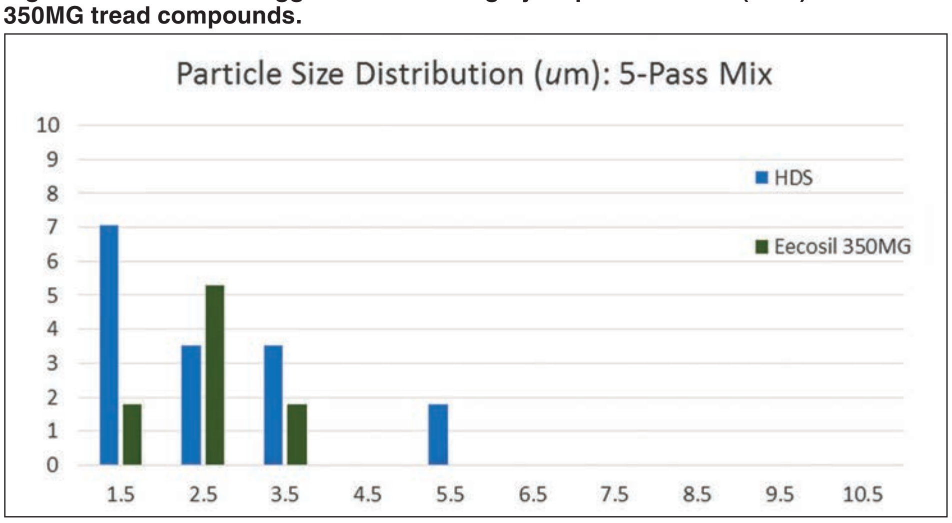

Fig. 16. Temperature sweeps for N234-control and three silica-filled treads for 5-Pass Mixes.

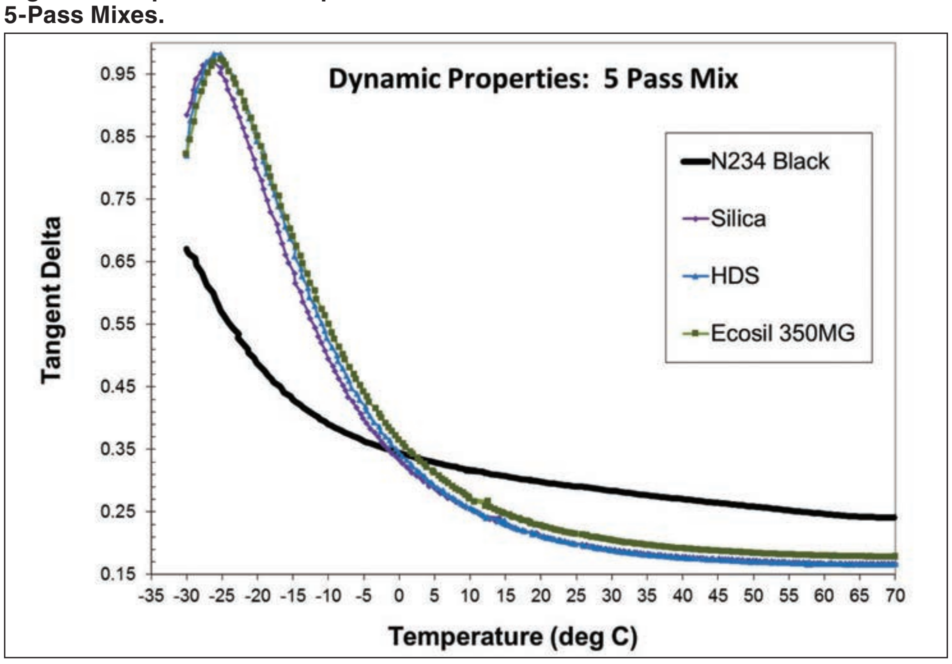

Fig. 17. Temperature sweeps for N234-control, HDS and Eecosil-filled treads for 3-pass and 5-pass mixes.

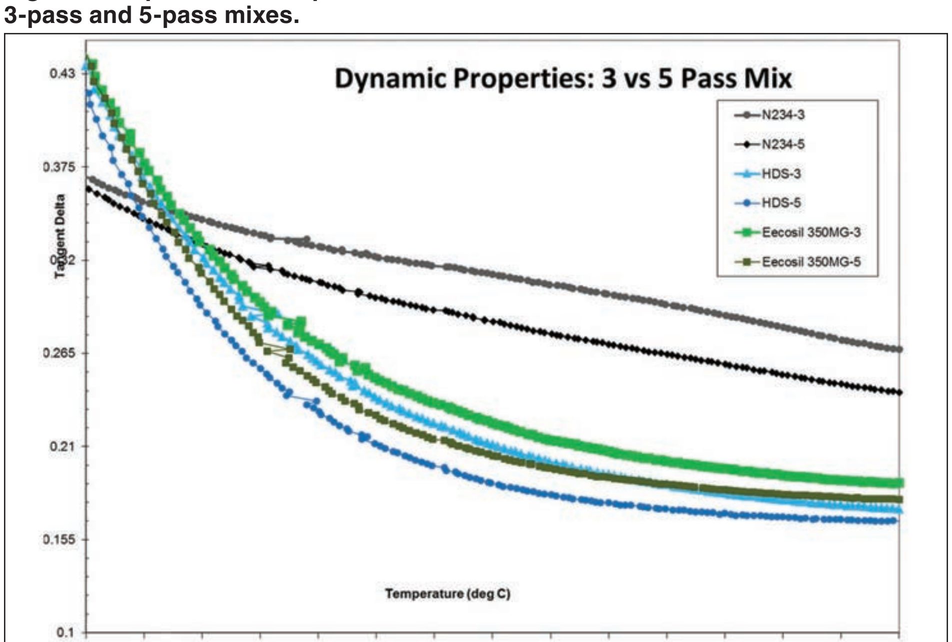

Fig. 18. Temperature sweeps for N234-control and silica-filled treads.

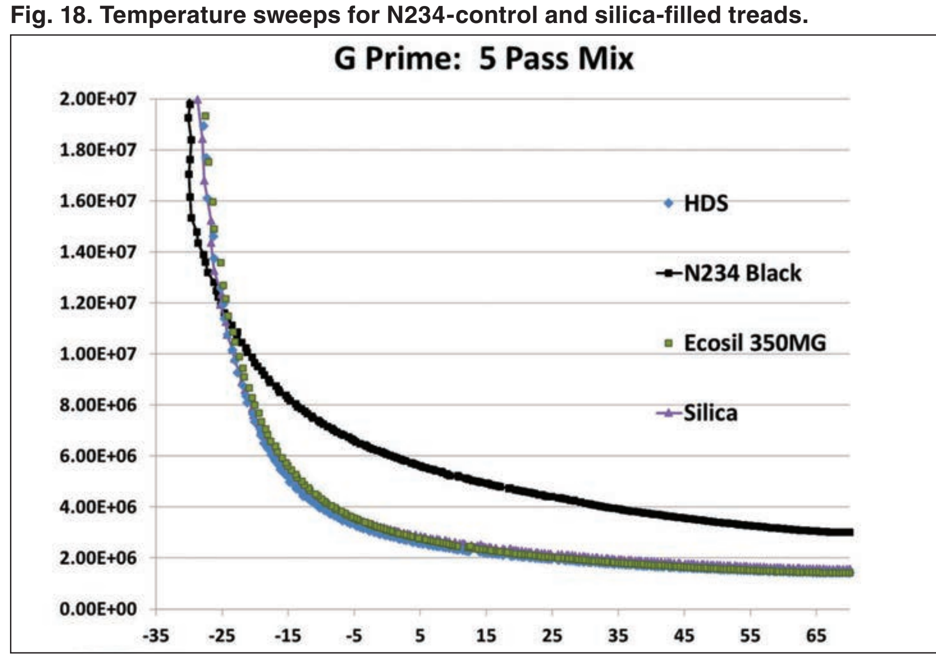

Fig. 19. Radar graph of important physical properties for silica-filled treads compared to the HDS compound, which is assigned a 1.0 value.

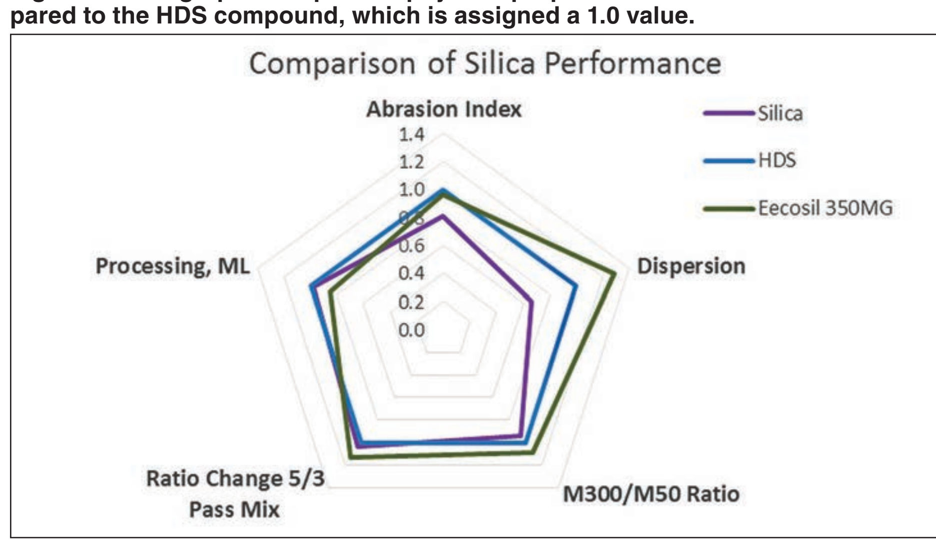

Fig. 20. Radar graph of important dynamic properties for silica-filled treads compared to the HDS compound, which is assigned a 1.0 value.