

Technical

How market drivers fuel tire additive innovations

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The auto market is rapidly changing, so tire innovation must never slow down.

"The automotive industry is changing faster than at any other time in history," according to James A. Popio, vice president of North America for Smithers Rapra. Speaking at the 34th Clemson Univer-

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sity Global Tire Industry Conference earlier this year,¹ Popio continued: "The future is not clear, so we must be ready for any number of scenarios."

The impact of changing market trends and regulatory demands also has been a recurring theme throughout a recent series of *Rubber & Plastics News* special reports titled "Game Changing Technology." In a future where fleets of autonomous, electric-powered

sport-utility vehicles could be the norm, where do tire manufacturers go for a secure and reliable pipeline of innovative material technologies?

Tire makers will rely on advances in compounds and processes to help prepare for demands ranging from increased load-bearing capacity for heavy batteries in electric vehicles, to greater fuel efficiency in fleets, to performance characteristics such as improved wet grip and longer service life.

Tire makers will be challenged with adopting these changes while producing these advanced tires efficiently and profitably. They must be prepared to adapt their processes and the material solutions they choose.

Meanwhile, developers of new material technology are challenged with rapidly translating these market drivers into solutions that meet customers' needs for rigorous testing, high-quality products, and reliability of supply.

This paper looks at four ways that innovations in tire additives directly impact a tire maker's ability to keep

pace with a changing market:

- Improved productivity in rubber processing;

Executive summary

Tire makers are challenged with satisfying the changing demands for fuel efficiency, improved performance and durability—all without negatively impacting operational productivity and cost.

This paper focuses on connecting market drivers and trends with material solutions that can help manufacturers improve operations, increase sustainability and enhance performance. Working from the Eastman Technology Center of Excellence in Akron, Eastman Chemical Co. collaborates with tire makers around the world to focus on innovations in insoluble sulfur, stabilizers, and performance resins.

Data presented in this paper highlight progress toward optimizing the balance of rolling resistance, wet grip and wear, while improving manufacturing outcomes in calendar speed and reduced bloom events. Results included here demonstrate how research, testing and material choices help the industry keep pace with market trends and preview unique solutions for the future.

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Fred Ignatz-Hoover is a technology fellow with Eastman Chemical Co. He has more than 30 years of experience working with accelerator and antidegradant chemistry, as well as carbon black dispersion.

He has worked with molecular modeling, applying semi-empirical quantum mechanical techniques and QSPR/QSAR techniques to various aspects of polymer chemistry and vulcanization chemistry. This modeling work has brought new insights into the mechanism of zinc-mediated-accelerated sulfur vulcanization and free radical reactivity in antidegradant chemistry.

Ignatz-Hoover earned his doctorate from the University of Akron. He is a member of the ACS Rubber Division, and was the recipient of the Rubber Division's Melvin Mooney Award. He has served as editor of *Rubber Chemistry and Technology* and is an inaugural member of the Advisor Board at the Florida Center for Heterocyclic Compounds at the University of Florida, the Industrial Advisory Board for the Center of the Advanced Polymer Composites Engineering at Ohio State University, and the Industrial Advisor Board at the University of Akron's Department of Chemistry.

Mark Arigo is an associate scientist at Eastman in the Tire Additives Technology Division. He earned a bachelor's in mechanical engineering from the University of Pittsburgh, and his master's and doctorate degrees in engineering sciences from Harvard University, where he researched flow of polymeric fluids, rheology and materials science.

After a tenure in academia at the University of Pittsburgh, Arigo has worked in the rubber industry for 17 years at Bridgestone, Lion Copolymer and Eastman. Dur-

ing this time, his research has focused on polymer and materials development for tire and non-tire applications, and gaining fundamental insights into tire performance mechanisms such as rolling resistance, wet grip and wear.

Arigo holds several patents on innovative polymer microstructures and macrostructures, and polymer-silica composites. Currently, he conducts new application research for tires at Eastman, including developments on Impera-brand resins and Acena-brand cellulose esters.

Dominica Hiu Ching Wong is a senior chemist with Eastman's Tire Additives Technology Division in the Additives & Functional Products segment. While receiving her doctorate from the University of North Carolina in Chapel Hill, Wong published five publications and received numerous awards. Since joining Eastman in 2015, she has worked in research and scale-up chemistry and applications development in the polyester, chemical intermediates and tire additives technology platforms.

Leandro Forciniti is a senior application research scientist at Eastman. Forciniti began his career at Goodyear where he worked on rubber compounding for heavy truck tires and was a technical team leader in mixing and extrusion. Through his work at Goodyear, he was awarded 17 patents.

In his graduate work at University of Texas-Austin, Forciniti, who holds a doctorate, worked to develop tunable composite materials made of different polymeric chemistries for biomedical applications, publishing five publications with a total of 268 citations. He is a member of American Chemical Society and the ACS Rubber Division.

Fig. 1: Higher tensile strength and tighter distribution demonstrate better dispersion. Desired results can be achieved with shorter mixing times.

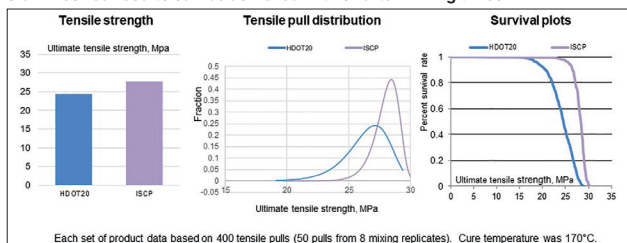
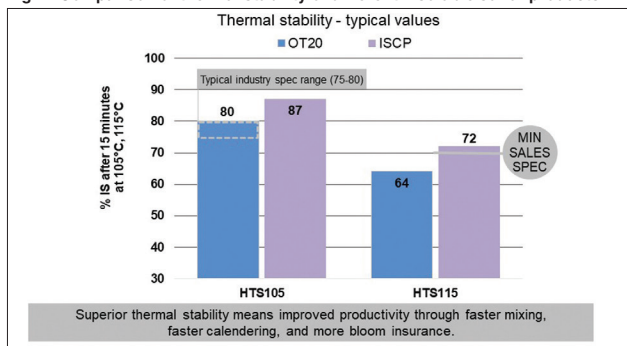


Fig. 2: Comparison of thermal stability of different insoluble sulfur products.



- Improved tire performance and safety;
- Improved tire durability; and
- Reliability of material supply.

Innovations for productivity

Whatever road the future takes, greater demands on tires and tire makers will require new, more advanced compounds and more complex tire portfolios. SKU proliferation is sure to increase as tire manufacturers accommodate a greater range of sizes, brands and performance characteristics. The goal for tire manufacturers is to refine processes and select materials that help to increase plant efficiency and produce more tires per shift while minimizing capital investments. This creates an even greater need for faster material handling, shorter mix times and increased calendaring speed, resulting in higher throughput and more favorable manufacturing economics.

Highly reinforced structural components of tires, hoses and other sulfur vulcanized articles require high modulus to achieve the necessary engineering stiffness for performance. In order to achieve such high moduli, high sulfur and often high filler loadings are required, achieving the desired final performance characteristics, but they also bring processing problems.

Using ordinary sulfur, S8, at levels above the solubility limit leads to the formation of bloom in inventoried rubber components. Bloom may contribute to poor building properties and/or result in composite products having low interply adhesion characteristics. Bloom events are costly both in terms of material loss and loss of production time. Reducing the risk of such events typically requires lowering temperature during processing, slowing down the processes, and negatively affecting productivity.

Polymeric sulfur, otherwise known as insoluble sulfur, has become an indispensable material in the manufacturing of high modulus rubber articles or components of tires, belts and hoses. Insoluble sulfur, as the name implies, does not dissolve and therefore does not bloom when used at high loadings. But it is necessary that at some point the sulfur must dissolve and diffuse into the rubber in order to participate in vulcanization.

Polymeric sulfur provides a convenient method to deliver sulfur into the compound in a non-blooming form which later, by thermal and by chemical mechanisms, depolymerizes to deliver rhombic or soluble sulfur (S8) required for vulcanization. The thermal lability of polymeric sulfur complicates processing because

processing temperatures should be low enough that depolymerization rates are slow, but should be as fast as safely possible to maximize manufacturing productivity.

Highly filled compounds especially those with low extender levels, exacerbate the problem with their inherently high viscosity. In addition, the chemical lability should be sufficient such that vulcanization kinetics of polymeric sulfur should be the same as those of conventional rhombic S8.

How can material selection help make processing faster and more reliable for tires, especially as formulations get more complex?

Improved dispersion

Faster dispersion during mixing enables greater flexibility of mixing times and speeds, allowing more batches to be produced in the same time with the same equipment. When undermixed, slow-dispersing insoluble sulfur products produce compounds that can have localized high sulfur concentrations.

High localized sulfur concentrations produce high modulus regions. These are critical flaws that can reduce mechanical properties of the rubber, including fatigue and tensile properties. Highly dispersible or faster dispersing insoluble sulfur allows for shorter processing time in order to reach the high levels of dispersion required for highly durable components.

Material scientists measure dispersion quality through size distribution of undispersed sulfur aggregates in uncured rubber and/or tensile strength characteristics of the cured rubber. The results presented in Fig. 1 compare insoluble sulfur with enhanced dispersion characteristics to the traditional industry standard. Improved dispersion delivers greater crosslink uniformity, resulting in improved tensile strength at comparable mixing conditions.

The combination of improved dispersion characteristics along with improved thermal stability translate into tangible benefits for tire manufacturers, enabling greater flexibility in mixing times and speeds. This allows more batches to be produced in the same time with the same equipment while often producing a more durable rubber component. These improved dispersion characteristics have been shown in plant-scale testing to reduce final mix time on the order of 10-25 percent.

Reduced mixing times because of improved additive dispersion also allow for real energy savings in one of the most energy-intensive portions of the tire making operation. With energy consumption in the mixing room accounting for an estimated one-third of the energy used in a tire plant, this operation is a natural place to look for improvements.

By reducing the duration of the productive mix by 10 percent, an

Fig. 3: How increasing thermal stability affects bloom risk, processing flexibility and productivity.

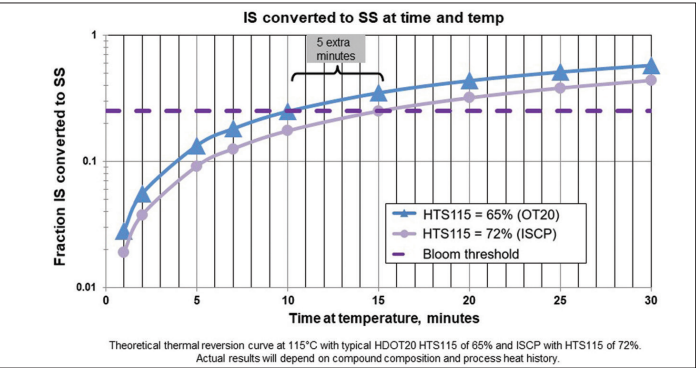


Fig. 4: Greater thermal stability results in less reversion to soluble sulfur during more aggressive mixing and calendaring conditions.

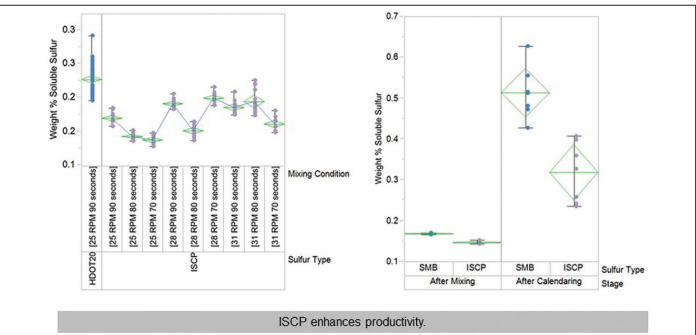


Table 1: Summary of observed melting behavior of sulfur allotropes.

Allotropic Sulfur Melting Points	
Allotrope	Melt
S6	88 ³
S7	39 ^{3,4}
α-S8	115, 112, 116 ^{3,4}
β-S8	119, 120, 121 ^{3,5,6,7,8}
γ-S8	109 ⁵
S-9	63 ⁹
S-10	92 ^{3,11}
S-11	74 ^{10,11}
S-12 (IS12)	148 ³
S-13	~90 ³
S-14	117 ^{12,13}
S-15	Non-reported
endo-S18	126-128 ¹⁴
S-20	121 ^{3,14,16}
S-μ	110 ³
Polymeric Sulfur	115-130

Table 2: Reversion of sulfurs to S8 at mixing temperatures.

Final Mixer Temperatures with % sulfur recovered as S8						
Compounds formulated with:	Conventional insoluble sulfur			IS12		
Target temperature	130	140	150	130	140	150
Actual temperature	131	137	151	131	139	146
% Cyclooctasulfur recovered	38.69	91.34	97.04	7.91	15.1	49.8

Tests compare thermal stability of IS12 (highlighted) with commercially available polymeric sulfur vulcanizing agents

average tire plant is positioned to eliminate hundreds of thousands of dollars in energy spend. These improvements in material technology are therefore going beyond contributions to product characteristics but are strong contributors to meet energy efficiency goals that are driven by both plant economics and trends toward more efficient manufacturing.

Thermal stability

While insoluble sulfur has been critical to tire making for decades, new industry demands and a competitive market environment drive companies to continue to seek better solutions. In turn, raw material suppliers are responding with new products, as seen in the recent addition of Crystex Cure Pro (ISCP) to the Eastman Crystex-brand insoluble sulfur portfolio. More heat is generated when mixing and calendering today's new compounds.

Lower rolling resistance and lightweighting are two of the desirable tire properties that require compounds that run hotter during processing, creating a greater risk of bloom events. Higher thermal stability insoluble sulfur can cut processing time and reduce scrapping of both rubber and steel, which can cost hundreds of thousands of dollars per bloom event.

ISCP provides lower conversion

to Rhombic sulfur compared to conventional insoluble sulfur processed at similar conditions. Mixing can be accomplished at higher rates (which generate higher compound temperatures) often with lower conversion to soluble sulfur. Since heat generation is often a limiting factor in calender speeds, ISCP allows higher calendering speeds often with lower conversion to sulfur.

ISCP was developed with improved thermal characteristics; the improved thermal stability properties are shown via the high thermal stability test in **Fig. 2** relative to the industry standard. **Fig. 2** shows the results of thermal stability testing after 15 minutes at 105°C and 115°C; the values reported are the percent remaining insoluble sulfur in the sample.

Fig. 3 charts the conversion of insoluble sulfur to soluble sulfur at 115°C using rate constant data derived from thermal stability testing. Lower values of soluble sulfur over time demonstrate ISCP's enhanced flexibility in processing insoluble sulfur containing compounds while managing soluble sulfur. This provides opportunity to mix longer and or calender faster (hotter) before reaching soluble sulfur levels approaching the bloom threshold. **Fig. 3** shows that ISCP provides

approximately five minutes of additional processing time, enabling opportunities for better distributive mixing.

Alternatively, the improved thermal characteristics would allow for processing (mixing, extrusion or calendering) at approximately 5°C hotter than traditional insoluble sulfur materials.

Sulfur masterbatch (SMB, a predispersed insoluble sulfur, often ~60-75 wt percent in a polymer binder) is often employed to deliver high dispersion of insoluble sulfur. Even at shorter mixing times, ISCP has exhibited dispersion qualities similar to that of a sulfur masterbatch, which includes predispersed insoluble sulfur but without the added cost and labor required by the SMB step.

A recent trial measured the reversion to soluble sulfur for ISCP and the industry standard. **Fig. 4** compares soluble sulfur levels of compounds containing ISCP in aggressive mixing with SMB containing compounds. Results demonstrate ISCP delivers lower soluble sulfur levels even with more aggressive mixing conditions. This knowledge can inform adjustments that reduce final mix time. It can also help achieve significant reduction in soluble sulfur relative to SMB. Accurate predictions from these tests en-

able control of process, chemistry, time and temperature.

Combining improvements with dispersion rate and thermal stability can result in significant improvements in plant mixing and calendering capacity. Plant scale mixing experiments have demonstrated improvements in mixing on the order of 10-25 percent and increases in calender speeds on the order of 10 percent, in many cases with lower conversion of insoluble sulfur to Rhombic sulfur.

In the pipeline

Material suppliers must always stay at least one generation ahead of their commercialized products to anticipate shifts in market drivers. For example, the makers of ISCP are testing and validating the performance of a novel new vulcanizing agent, cyclododecasulfur (IS12). In experimental stages, IS12 demonstrates thermodynamic stability at conventional rubber processing temperatures while having the same vulcanization characteristics as conventional insoluble sulfur or rhombic sulfur.

Thermal polymerization and depolymerization reactions of allotropes of sulfur have been well studied and reviewed.³⁻¹⁵ **Table 1** summarizes the observed melting behavior of various allotropes

Fig. 5: Consumer demand for safer tires is a global market driver. These examples highlight consumer awareness and regulatory trends.

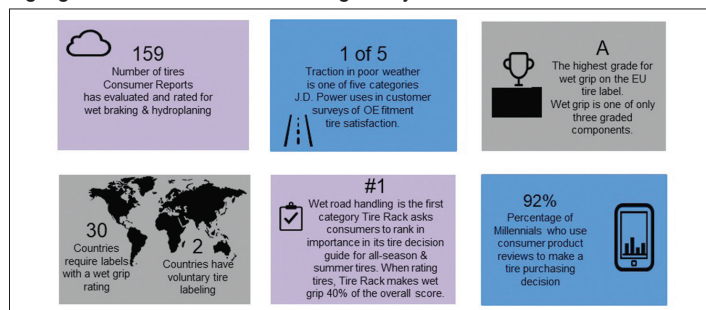


Fig. 6: Adding resins improves performance by significantly shifting T_g to higher temperatures.

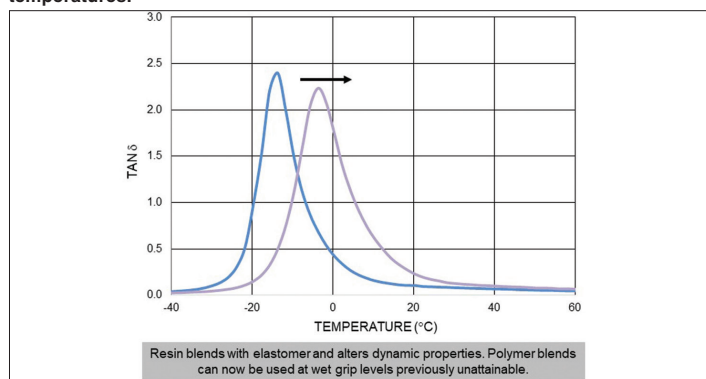


Fig. 7: Conventional methods to improve wet grip involve changing polymer blend ratios to achieve a higher T_g .

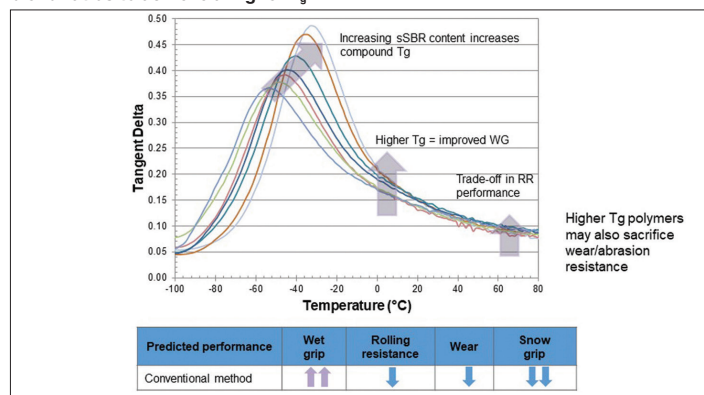
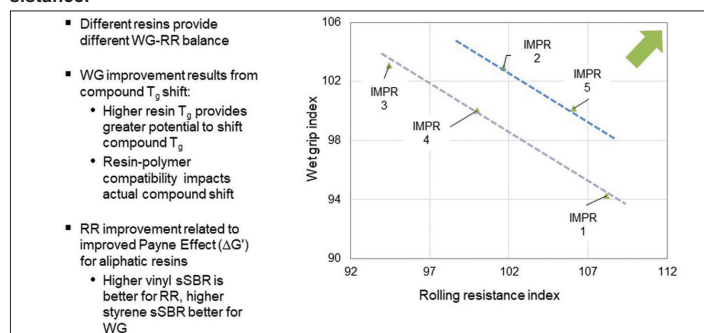


Fig. 8: Performance resins provide options for balancing wet grip and rolling resistance.



with IS12 exhibiting one of the highest melting points. As a result, its possible application to tire processing has been very appealing to rubber scientists.

Laboratory mixing tests compared the stability of fully formulated compounds containing IS12 or commercially available polymeric sulfur vulcanizing agents. The results in **Table 2** demonstrate IS12's marked reduction in reversion to cyclooctasulfur at mixing temperatures of 130°C, 140°C and 150°C.¹⁶

At the same time, this unexpected advantage of IS12 can be achieved without changing vulcanization kinetics. Masterbatches containing accelerators, N,N1-Dicyclohexyl-2-benzothiazole sulfenamide (DCBS), 2-mercaptobenzothiazole (MBT) or 2-mercaptobenzothiazole disulfide (MBTS) were mixed to achieve 5 phr active sulfur in each compound.

Nearly identical cure rates and cure parameters are observed for IS12, conventional insoluble sulfur and rhombic when vulcanized at various temperatures ranging from 130°C to 180°C.¹⁷ This is validated by comparable Arrhenius parameters, which demonstrate that the rate determining step in vulcanization is identical regardless of the choice of sulfur.¹⁷

With ISCP insoluble sulfur very significant improvements in productivity and cost savings are available today.

Innovations for performance, safety

In the future, tire brands will continue to face even greater demands to perform better, last longer and operate safely.

It will continue to be a challenge for tire compounders to simultaneously optimize wet grip (WG), rolling resistance (RR) and wear resistance included in the

traditional “magic triangle.” The goal is to expand the area under the triangle, but there are inherent viscoelastic tradeoffs associated with balancing WG-RR and WG-wear.

Performance resins are a useful compounding tool to expand the magic triangle so that compounders can optimize WG, RR and wear properties of tire tread compounds.

To address these challenges in a meaningful way, tire makers will need to evaluate the rubber additives they're using. Modern performance resins can help balance performance and safety without compromising the integrity of their manufacturing process. They also can help achieve compliance with emerging labeling and performance requirements.

Drive toward greater safety

The trends that are shaping consumer demand for safer tires are well-known: 30 countries require labels with a wet grip rating; “traction in poor weather” is one of only five categories J.D. Power uses in customer surveys of OE fitment tire satisfaction; “wet road handling” is the first category Tire Rack asks consumers to rank in its tire decision guide (and accounts for 40 percent of the overall score); and 92 percent of millennials use consumer product reviews to make a tire purchasing decision (**Fig. 5**). These trends underscore the importance of wet grip as a desired performance property.

In addition to reviews by Consumer Reports, J.D. Power and

Fig. 9: Performance resins have been used to improve the balance of wet grip and wear.

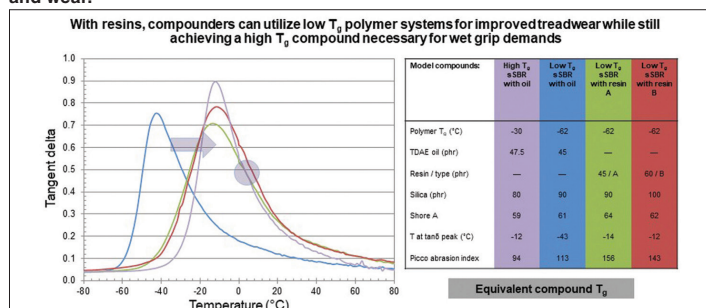


Fig. 10: Belt edge separation and chip-chunk damage are two of the unmet needs identified by the trucking industry. Reversion resistance aids could address both needs.

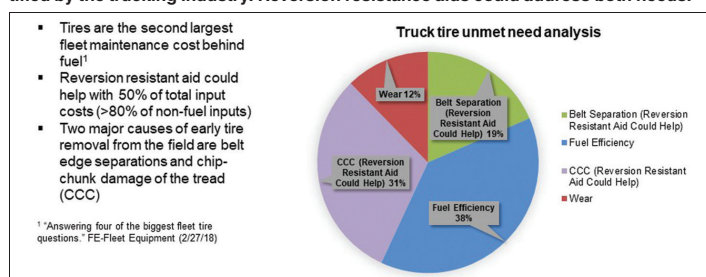


Fig. 11: Post-vulcanization stabilizers promote development of hybrid crosslink for longer flexible crosslink for greater flex-fatigue performance while increasing the percent of disulfidic crosslinks.

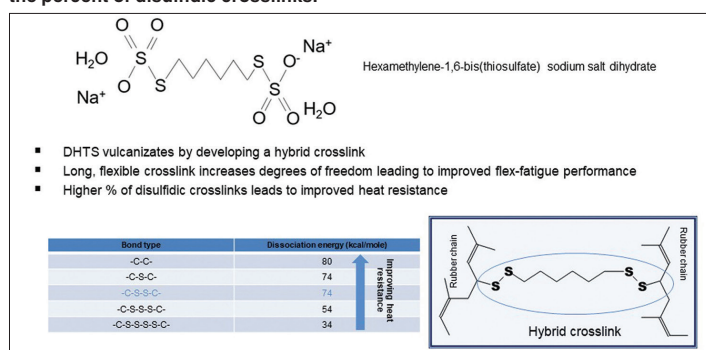


Fig. 12: Reversion resistant aids reduce reversion of crosslinks, even upon high thermal conditions.

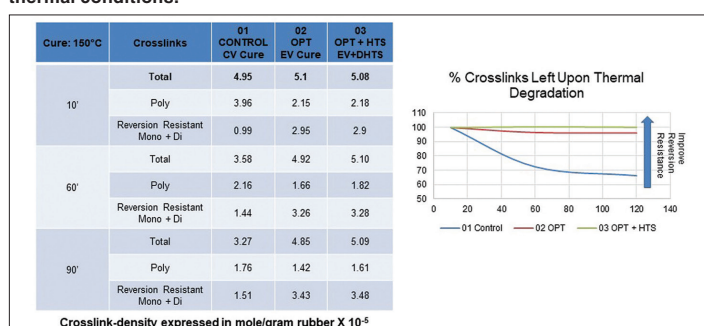


Fig. 13: Thermal reversion can improve blow values, according to Goodrich blow-out data.

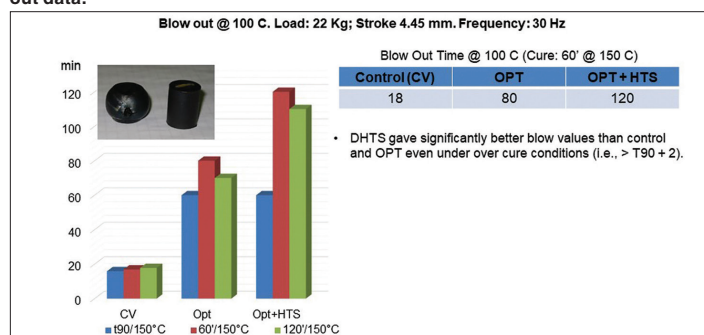


Table 3: Model steel skim formulation with cobalt salt and partial replacement of cobalt salt with DHTS.

Material	Baseline formulation	Partial Substitution 1	Partial Substitution 2	Negative Control
SIR - 10	100	100	100	100
N326	68	68	68	68
Stearic acid	2	2	2	2
Santolux™ antidegradant (6PPD)	2	2	2	2
TMQ	0.7	0.7	0.7	0.7
Naphthenic oil (Calsol 8240)	3	3	3	3
Impera 1507	3	3	3	3
Cobalt Neodecanoate (20.5% Co)	1	0.5	0.25	0
Duralink™ HTS	0	0.5	0.75	0
ZnO	8	8	8	8
Crystex™ insoluble sulfur	5	5	5	5
DCBS	1.2	1.2	1.2	1.2

Tire Rack, it's evident that wet grip is a key element of the global trend toward tire labeling, which is driving many compound reformulations. Around the world, a significant and growing number of countries require tires to carry labels with a wet grip rating, offering consumers a clear signal of the tire's traction and stopping ability on wet roads.

Labels are increasingly a source of consumer education about the importance of wet grip, and ongoing trends are expanding the conversation beyond WG to RR and wear.

Tire makers will need to improve wet grip to comply—and they will need to intensify their efforts to find tire additives that help them balance desirable properties in a way that differentiates their brands.

How resins improve wet grip

Resins are unique in that they are relatively small molecules (low molecular weight) but have a relatively high T_g compared to process oils used in treads. Res-

ins blend with elastomers and alter the dynamic properties of the compound. They are among the few additives that have a high T_g (>20°C) plus potential compatibility with the tire polymer system (SBR, BR and/or NR).

Compatible resins have the ability to “shift” and “broaden” the T_g of the compound, depending on resin attributes and compatibility with elastomers in the compound. By shifting the T_g to higher temperature, the wet grip indicator (higher $\tan\delta$ @ 0°C) is improved. This shift is represented in **Fig. 6**.

Conventional methods to achieve better WG involve using different polymer blends by adjusting the S-SBR/BR ratio, for example. However, these methods come with many tradeoffs in other performance dimensions, especially RR. **Fig. 7** shows these conventional methods as well as the predicted performance trade-offs. A second conventional method is to utilize increased filler loading, or different surface area fillers. This is certainly a valid strategy but also has its own im-

pact on WG-RR and wear balance.

Resins provide greater compounding flexibility by achieving compound T_g ranges that are inaccessible with polymer choice alone. They also help reduce trade-offs in RR.

To achieve the desirable WG-RR balance, it is critical to understand the properties that impact polymer-resin compatibility. If the resin is incompatible or partially incompatible in the compound polymer system, then phase separated resin domains can form. This results in less compound T_g shift (lower WG benefit) and increased high temperature hysteresis (worse RR).

Resin chemistry (C5, C9, or pure monomer) can change the aromatic or aliphatic property of the resin and influence the compatibility with polymer systems such as butadiene rubber, natural rubber and styrene-butadiene rubber used in tire compounds. Furthermore, it has been observed that more aliphatic resins can improve RR by means of reducing the Payne Effect (filler-filler interaction).

Using resins to optimize WG and RR in compounds requires careful consideration of the polymer-filler-resin system. For example, **Fig. 8** which compares five grades of Eastman Impera-brand performance resins in a silica-filled SBR/BR (20 percent styrene, 58 percent vinyl SBR) polymer blend compound.

How resins can improve wear

The advanced compounds of future tires will continue to drive toward the ideal balance in the magic triangle. To this end, scientists are intensifying research into how resins can be used to fine-tune compounds that deliver improved wear.

For example, low T_g polymers are known to have superior abra-

sion resistance (treadwear) compared to high T_g polymers.¹⁸ However, these low T_g polymers may compromise WG performance in the tread. Performance resin research is demonstrating that compounders can utilize low T_g polymer systems for improved treadwear while still achieving a high T_g compound necessary for the market need for improved wet grip.

Fig. 9 compares a high T_g SBR compound without resin to three compounds with a low T_g SBR: no resin, 45 phr of Resin A and 60 phr of Resin B. In this case, the resin is used to increase the compound T_g to match the high T_g SBR compound. The lab test results indicate similar WG performance, but significantly improved abrasion resistance for the resin compounds.

It is observed that resins often improve abrasion resistance in rubber compounds. Testing has found that resins increase the viscous loss modulus (G'') at high strain. Higher G'' means more energy is dissipated at high strain, and less energy is available to tear or abrade the elastomers.

A delicate balancing act is required for compounding with resins to optimize WG, RR and wear without compromising the manufacturing process. This challenge underscores the importance of approaching tire performance compounding with both technical expertise and a broad resin portfolio.

Innovations for greater durability

Longer life will continue to be critical for tires in the future. Tomorrow's environment will include new challenges such as more stringent government regulations, the growth of electric vehicles whose heavy batteries require higher load ratings and many more. This is especially

Fig. 14: Partial cobalt salt replacement with DHTS in steel skim formulation give equal steel cord adhesion pullout forces with similar coverage.

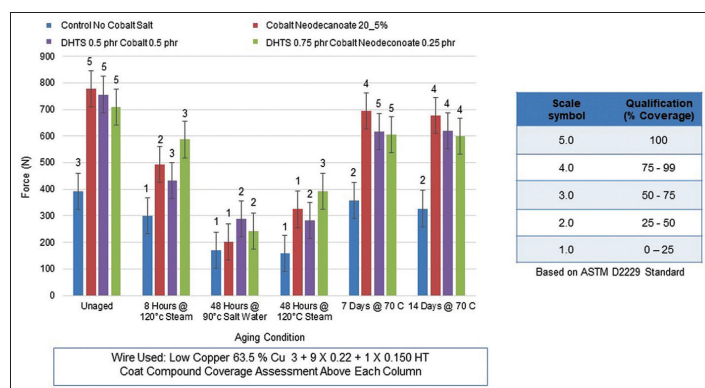
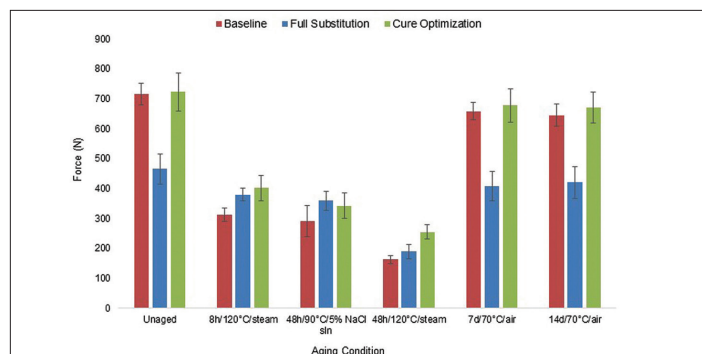


Table 4: Model steel skim formulations with DHTS and cure adjustment to give equal cure state as cobalt control.

Material	Baseline formulation	Full substitution	Cure optimization
SIR - 10	100	100	100
N326	68	68	68
Stearic acid	2	2	3.0
Santoflex™ antidegradant (6PPD)	2	2	2
TMQ	0.7	0.7	0.7
Naphthenic oil (Calsol 8240)	3	3	3
IMPR 1507	3	3	3
Cobalt Neodecanoate (20.5% Co)	1	0	0
DHTS	0	1	1.5
ZnO	8	8	8
ISCP	5	5	4.5
DCBS	1.2	1.2	1.2
Onset of Cure (Ts1)	1.620	2.460	1.67
T25	4.70	4.69	4.72
T90	12.19	15.01	12.15
Delta Torque	24.25	20.75	24.75
Modulus 300%	16.01	14.91	16.52

Fig. 15: Full cobalt salt replacement with DHTS and cure adjustments give equal steel cord adhesion pullout forces.



true in the heavy trucking market where the cost of tire replacement is second only to fuel as the greatest operating cost.²⁰

Tire makers need additives that help improve tire building and ensure long tread life. And they need it from a source that is reliable and sustainable down the road.

Reversion resistance

The market's demand for longer life and higher load ratings has led Eastman to conduct application research to find the best way for tire makers to use current technology. In addition, the insights from these discoveries has provided focus into what the next generation reversion-resistant chemistries need to be.

According to a leading trucking publication,²⁰ two major causes of early tire removal from truck fleets are belt edge separations and chip-chunk damage (Fig. 10). Reversion plays a key role in both causes.

Additives such as Eastman Duralink-brand HTS post-vulcanization stabilizer (DHTS) enhance steel-cord adhesion in aggressive environments, but also may improve durability by reducing belt edge separations and chip-chunk damage of the tread.

By generating hybrid crosslinks (Fig. 11) in the vulcanization process, reversion resistance aids such as DHTS also increase the degree of flex freedom leading to improved flex-fatigue performance and reduced tear. Because of its network preservation, DHTS also maintains dynamic stiffness in tread caps and bases in heavy truck tires to reduce heat build-up and hysteresis.

DHTS demonstrates improved thermal stability as measured by MDR, versus control (CV cure) and an EV cure option. Cure data at 150°C demonstrates faster cure kinetics, higher cure state and improved thermal stability. This is supported by sulfur rank analysis on samples cured for different times, including over-cure conditions. Fig. 12 shows significantly higher reversion resistant crosslinks (mono + di-sulfide crosslinks), even upon high thermal conditions.

Using Goodrich blowout data, rubber components with improved reversion demonstrate significantly better blow values than controls resistance (Fig. 13), even when exposed to over-cure conditions (>T90 + 2). In this and other

testing, DHTS delivered these results with competitive fatigue properties and no impact on wear performance or heat generation.

The addition of this post-vulcanization stabilizer can offer greater network stability on reversion and heat stability during typical operating conditions. This can improve fatigue resistance and tear strength, even under over-cure conditions, and significantly improve storage modulus and abrasion resistance.

Sustainable cobalt replacement

Cobalt salts are a traditional solution for steel cord adhesion. Cobalt salts primarily act to inhibit dezincification by acting as an interstitial site dopant in the CuZn lattice network.

Recently, there has been a rapidly increasing demand for cobalt to serve the lithium ion battery market, especially for growing numbers of electric vehicles. In addition to rising prices and tightening supplies of cobalt, a further concern for rubber users is instability in the cobalt supply chain, with the majority of this key raw material originating in the Democratic Republic of Congo.

A rising price environment and an unreliable source of a key ingredient will definitely drive changes in the tire market. Tire makers have shown that DHTS, in addition to providing an excellent reversion resistance aid, can partially or fully substitute cobalt salts in typical steel cord formulation with equal or improved steel cord adhesion in both unaged, aged and corrosive environments.

DHTS does this by replacing a large percentage of the thermally unstable polysulfidic bonds with a more thermally stable di-sulfide hybrid crosslink while still providing the flexible bond needed for steel cord application. A typical steel skim formulation can be seen in Table 3. Results from this type of formulation showed that most of the cobalt salts could be replaced with DHTS (Fig. 14).

This replacement can be achieved without adjustment to the fatty acid content or the resultant cure package. Table 4 presents a formulation with adjustment to fatty acid and resultant cure package that demonstrate modulus at 300 percent and T90 can be matched with control containing cobalt salts. With further

modifications to the formula through adjusting fatty acid content, full replacement of cobalt salts may be possible (Fig. 15).

Reliable material supply

In addition to product enhancement and differentiation, tire additive innovators must ensure reliable supply of their products and technical support around the globe.

Growing concerns that will drive markets around the world will include:

- Barriers to trade;
- Strained supply chains;
- Increasing regulation of transport; and
- Shortages of truck drivers in North America

Therefore, tire makers are looking for suppliers that are able to serve them with robust operations in multiple regions, and supply chains that are accustomed to handling huge and complicated volumes.

Tire makers will look for suppliers that are committed to the tire industry, with application-specific research capability and the deep underlying technology to solve problems. Successful suppliers will continue to have a long-term perspective that makes investments to satisfy current demand and future innovation.

Conclusion

Tire makers will face many challenges as they aim to deliver higher performing products and enhance productivity in this dynamic market environment. Fortunately, talented chemists, engineers and material scientists are discovering and optimizing new technologies to address these changes and anticipate future trends. These additive innovations will help the industry keep pace with market changes and move into the future with confidence.

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