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L. Brüggemann GmbH & Co. KG has a long history as a supplier to the rubber industry, primarily of high surface area zinc oxides for rubber compounds. Brüggemann established a rubber development laboratory in 2012 to create new solutions using its unique capabilities in the emulsion polymer, zinc, rubber and polymer additive industries. The main activities in this laboratory include data generation, product development and custom testing. This article will focus on the following topics, part of ongoing work in Brüggemann's rubber development laboratory:

- Reactive extrusion products/benefits
- Elimination of resorcinol/cobalt from steel cord compounds: TP 1862
- Formaldehyde reduction during processing: LP 21-103
- Resorcinol and cobalt (Re/Co) free low formaldehyde compound performance: TP 1862 + LP 21-103

Figure 1 - typical form of a reactive extrusion product, a non-dusting, non-hygroscopic, free flowing granule

Reactive extrusion products/benefits

An early focus of Brüggemann's work was in the field of reactive extrusion products. Utilizing a low melting point carrier compatible with rubber compounds, this technology combines multiple components into a single granular form. It enables the following benefits and attributes:

- Reduced number of items in a recipe
- Pre-dispersed/pre-activated/dust-free/ready-to-use granules
- Faster mixing
- Scavenging of hazardous substances (e.g., formaldehyde)
- Better handling and processing of highly active materials
- Lower dosage potential
- Encapsulated components with low or no VOC release

Figure 1 shows the typical form of a reactive extrusion product, a non-dusting, non-hygroscopic, free flowing granule.

Figure 2 illustrates several different concepts of reactive extrusion products and functions. There are three main types of reactive extrusion products:

- Pre-dispersion enables better distribution of a difficult to mix product in a compound. It is also useful for ingredients that are shear sensitive, as low mixing forces can be used to incorporate the ingredient in a carrier that is more easily

Figure 2 - several different concepts of reactive extrusion products and functions

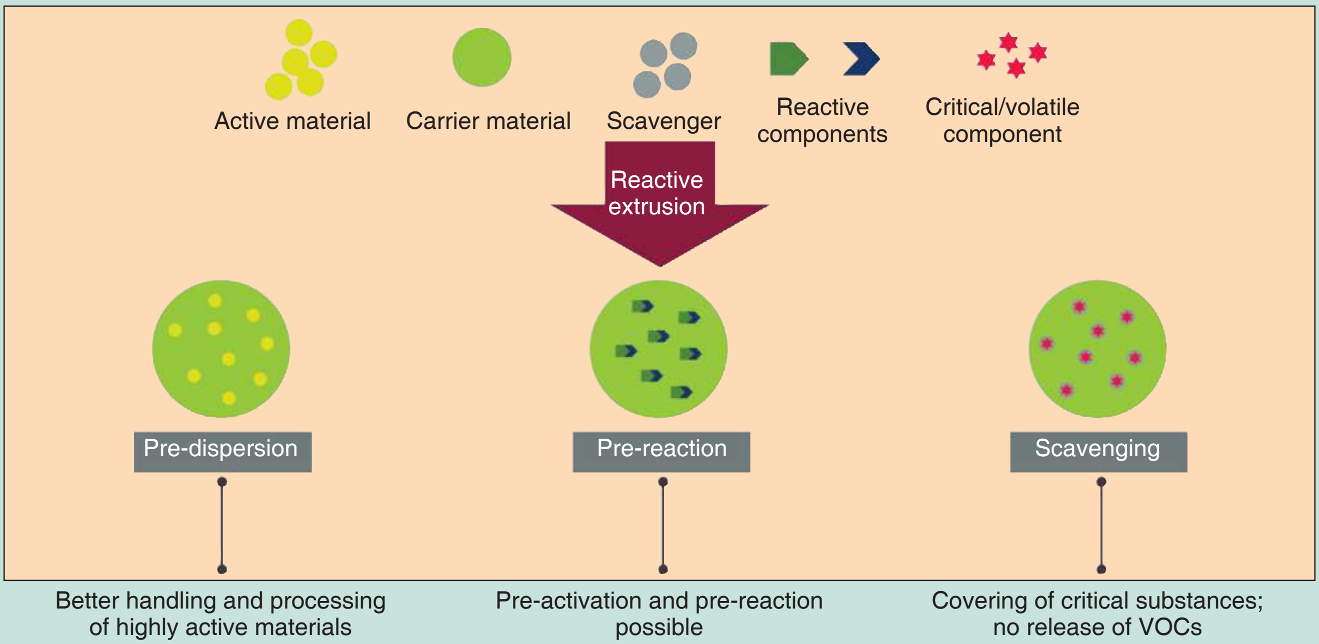
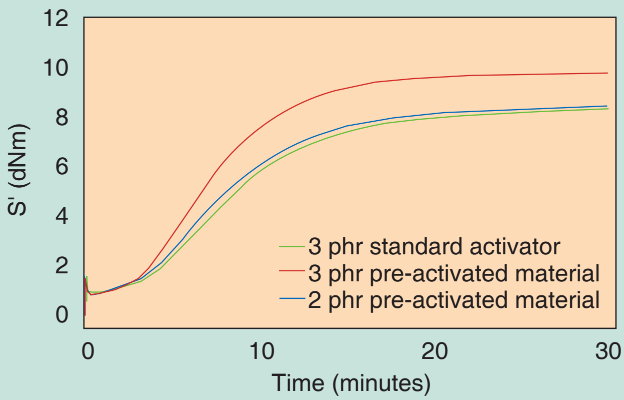


Figure 3 - a significantly lower dosage of a pre-activated material provides equivalent performance to a standard activator



dispersed in compounding (see figure 4 regarding TP 1850 and how it improves zinc oxide distribution).

- Pre-reaction, for example, can include mixing two components that will react under specific conditions, such as elevated temperature or shear force. In this example, reactive extrusion technology would initiate the desired pre-reaction between the components.
- Scavenging provides for "capture" or removal of an offensive component at any step of rubber compounding or vulcanization (see the section on formaldehyde reduction during processing, where LP 21-103, as a scavenger example, prevents release of formaldehyde).

Figure 3 shows that a significantly lower dosage of a pre-activated material provides equivalent performance to a standard activator. More uniform mixing of the pre-activiated material in compounding is possible, providing better dispersion and enabling better availability of all ingredients in the rubber compound.

Figure 4 shows better mixing with TP 1850, a pre-dispersion of an active zinc powder into a carrier. The image on the left shows conventional zinc oxide powder and dispersion at a given time. The picture on the right illustrates better dispersion of TP 1850 at the same mixing time. A summary of the benefits of reactive extrusion products is shown in table 1.

Figure 4 - better mixing is seen with TP 1850, a pre-dispersion of an active zinc powder into a carrier (right) versus a conventional zinc oxide powder (left) at a given time

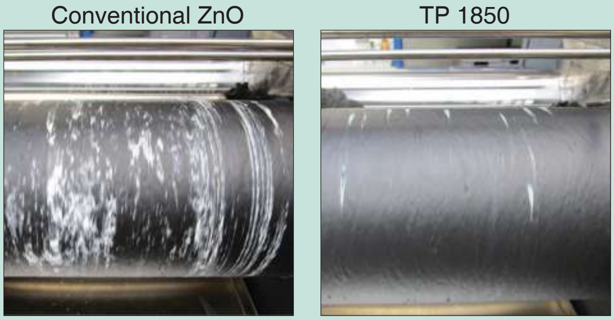


Table 1 - summary of reactive extrusion benefits

	Powder	*Prepacks*	*Rubber batched materials*	*Reactive extrusion technology materials*
Dust-free	-	+	+	+
Handling/ automation	-	(+)	+	+
Agglomeration prevention	-	-	+	+
Pre-dispersion	-	-	+	+
Broad compatibility of carrier	n/a	(+)	(+)	+
Pre-reaction	-	-	-	+
Covering of critical substances	-	-	-	+

Elimination of resorcinal/cobalt from steel cord compounds: TP 1862

Resorcinol and cobalt (Re/Co) have a long history of demonstrated performance to enhance rubber-to-metal bonding. They are widely used in tire compounds to ensure long term steel cord adhesion. However, ongoing toxicology concerns about resorcinol initiated by Finland and France indicate it is a potential endocrine disruptor with high aggregated tonnage use (ref. 1). The European Commission (ECHA) recently put forth a proposal to list resorcinol as a substance of very high concern (SVHC) (ref. 2). These recent developments indicate a need for an alternate sustainable solution to remove resorcinol from rubber compounds.

Cobalt supply chain and toxicity concerns reveal a need to develop rubber-to-metal bonding solutions without this ingredient, as well. TP 1862 has been developed and demonstrates equivalent performance to rubber compounds containing Re/Co.

TP 1862 is a ready-to-use masterbatch in granule form. It is a Re/Co-free resin system based on a novolac, doped with activated zinc ions. This combination of a resin with highly active zinc achieves high mechanical strength, while maintaining adhesion to steel. Aging processes can be reduced due to the high availability of activated zinc. Crucial properties of a tire adhesion mixture are obtained without Re/Co. A positive side effect of the newly developed product is that the use of ZnO is no longer necessary; zinc contained in the masterbatch additionally acts as a vulcanization activator. In addition to the elimination of Re/Co, it is also possible to significantly reduce the amount of heavy metal zinc needed in a tire compound.

For the following figures and table 2, all mixtures were produced with a 1.6 liter internal mixer, and were further processed on a 150 mm roller mill. Vulcanization characteristics were analyzed via a moving die rheometer (MDR) at a temperature of

Table 2 - typical tire reference compound and alternate Re/Co-free recipes

Reference compound	*(phr)*	*TP 1862*	*(phr)*
NR	100	NR	100
N326	55	N326	55
Stearic acid	2	Stearic acid	2
Silica	15	Silica	15
TMQ	1	TMQ	1
Oil	4	Oil	4
Resorcinol[1]	3	-	-
Cobalt salt[2]	0.75	TP 1862	8.5
ZnO[3]	6	-	-
HMMM	4	HMMM	4
Sulfur	6	Sulfur	6
DCBS	0.6	DCBS	0.6
TBBS	0.9	TBBS	0.9

1. Pure reagent grade
2. ECOS S 9.3 (Co 9.3% stearate)
3. Red seal type

* TBBS is an essential ingredient in this compound

155°C. The mixtures were each vulcanized to t95 on a 400 kN laboratory press. Test specimens were obtained from the finished rubber sheets for the measurement of tensile values, hardness, rebound resilience and compression set. Brass coated steel cord (Bekaert 2 + 2 x 0.25 HT, 63.5% Cu) was used and incorporated into the vulcanized rubber to determine the adhesion properties. All mechanical values as well as rheometer curves were recorded several times to ensure reproducibility. Values shown in each figure are average values of at least 3-5 individual measurements. Standard deviation is not significant in all cases, and is therefore not shown for clarity reasons.

Figure 5 - rheometer result comparisons of compounds with improved results for the TP 1862 compound

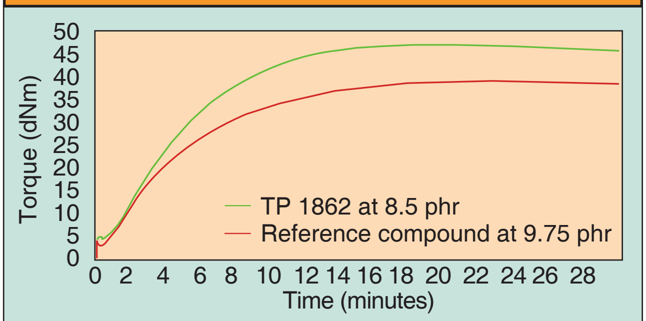


Figure 6 - additional property comparisons of the two compounds

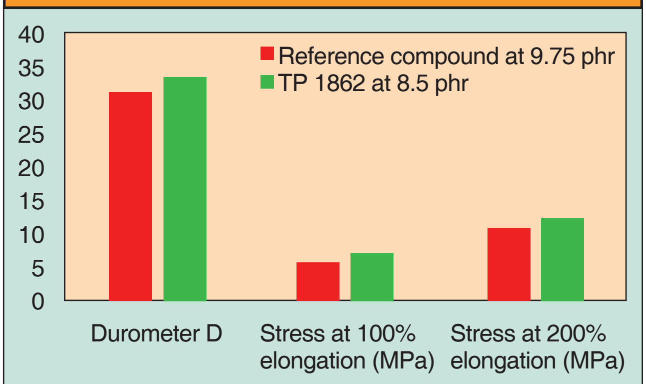


Figure 7 - pull out force (POF) of a steel cord in the compound 24 hours after vulcanization

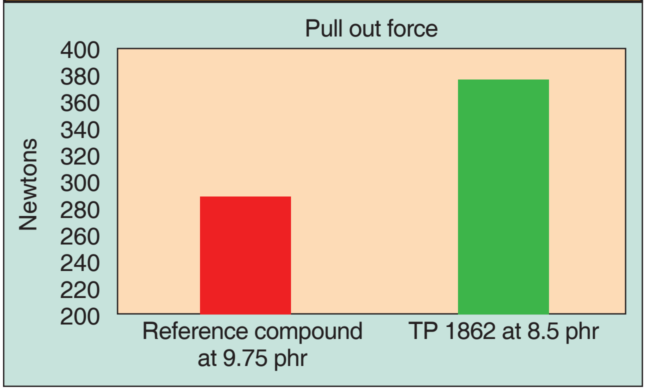


Figure 8 - heat aging differences between the reference compound and TP 1862

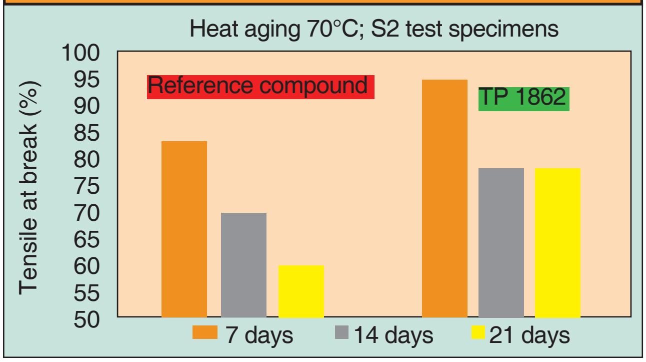


Table 2 shows a typical tire reference compound and alternate Re/Co free recipes. Note that TP 1862, one ingredient, replaces three ingredients: resorcinol, cobalt and zinc oxide. Subsequent figures show how these two compounds compare when subjected to typical rubber compound testing.

Figure 5 shows rheometer result comparisons of these compounds, with improved results for the TP 1862 compound. Higher crosslinking density is achieved earlier in vulcanization, as well as significantly higher values at the end.

Figure 6 shows additional property comparisons of the two compounds. Improvements are observed in durometer D hardness, as well as stress at both 100% and 200% elongation.

Figure 7 shows pull out force (POF) of a steel cord in the compound 24 hours after vulcanization. TP 1862 shows a more than 30% improvement versus the reference compound.

Figure 8 reveals heat aging differences between the reference compound and TP 1862. Improvements are shown initially and at each interval tested. After 21 days, TP 1862 showed 28% higher tensile strength versus the reference compound.

Figure 9 - steel cord POF retention values for 90°C water aged samples

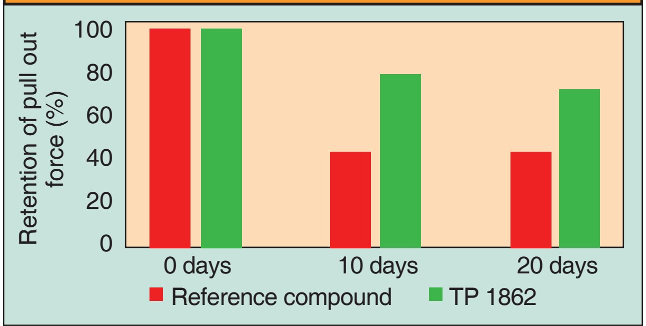


Figure 10 - steel cord coverage values after 90°C water aging

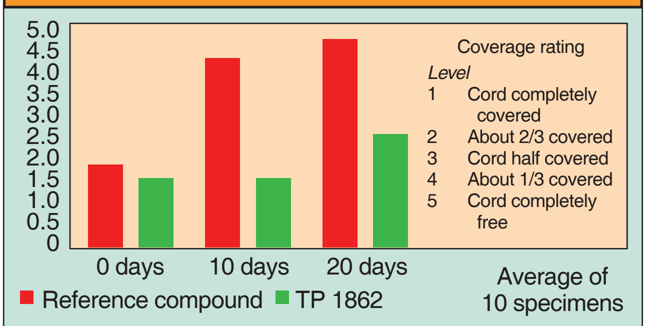
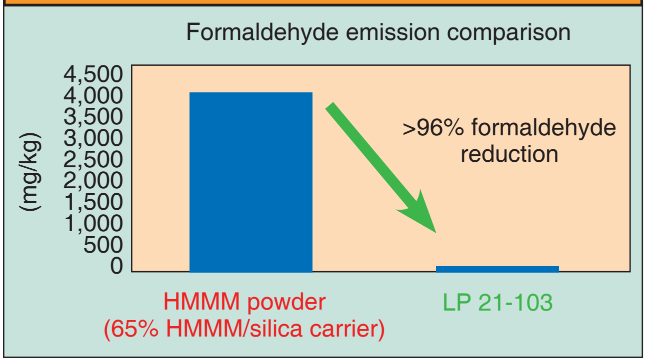


Figure 9 shows steel cord POF retention values for 90°C water aged samples. Both compounds show the same initial results, but TP 1862 shows a more than 50% improvement versus the reference compound after 20 days.

Figure 10 shows steel cord coverage values after 90°C water aging. In this subjective dimensionless test, TP 1862 scores significantly higher. Figure 11 contains images after pull out of rubber retention on the steel cord, both dry and after water aging,

As shown in figures 5-11, compounds formulated with TP 1862 outperform those formulated with Re/Co ingredients. A sustainable solution for robust metal bonding of rubber to steel tire cord free of Re/Co content is available. This product is provided in free flowing granules and enables improved performance, a reduced number of components in a compound and easier processing.

Figure 12 - formaldehyde release is compared when LP 21-103 is substituted for HMMM powder in a typical Re/Co rubber compound



Formaldehyde reduction during processing: LP 21-103

Hexamethoxymethylmelamine (HMMM) is widely used in the rubber industry, with a long history of proven performance. However, HMMM is known to release formaldehyde during processing. Formaldehyde is classified as a human carcinogen. Short term exposure to high levels can be fatal, and long term exposure can cause respiratory difficulty, exzema and sensitization (ref. 3). It is prudent to reduce formaldehyde emissions where possible. These needs have led to the development of a reactive extrusion scavenger for formaldehyde: LP 21-103. Initial testing of LP 21-103 was performed with the reference compund using a Re/Co additive.

Figure 12 compares formaldehyde release when LP 21-103 is substituted for HMMM powder in a typical Re/Co rubber compound. Formaldehyde emission is reduced by more than 96%.

Figure 13 shows a recipe and rheometry comparison of compounds with HMMM and LP 21-103.

Figure 14 shows a performance comparison after vulcanization of these compounds, showing nearly identical performance for all tested items, such as torque, scorch time, hardness, pull out force and cord coverage. Application testing of compounds produced with LP 21-103 has shown no performance deficiencies compared to a reference compound.

By substituting LP 21-103 for HMMM, nearly all formaldehyde can be eliminated during processing, with no performance degradation of the vulcanized rubber compound.

Figure 11 - images after pull out of rubber retention on the steel cord, both dry and after water aging

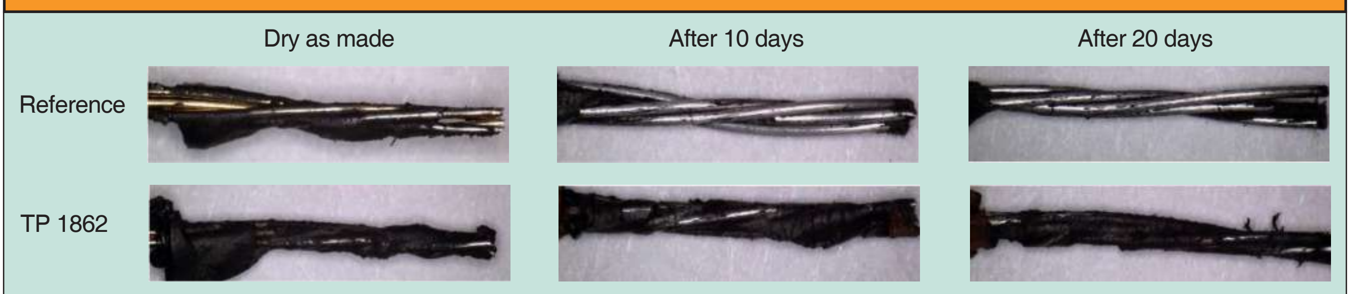


Figure 13 - recipe and rheometry comparison of compounds with HMMM and LP 21-103

LP 21-103 versus HMMM in a Re/Co formulation

Ingredients	*phr*	
Natural rubber	100	100
Carbon black N326	55	55
Palmera B 1805 pastillen	2	2
Silica (Evonik VN3)	15	15
TMQ	1	1
Petronas process oil N 100	4	4
ZnO red seal	6	5
Cobalt salt (ECOS S 9.3)	0.75	0.75
Resorcinol	3	3
HMMM powder	4.15	0
LP 21-103	0	6
Crystex-HD-OT-20	6	6
DCBS	0.6	0.6

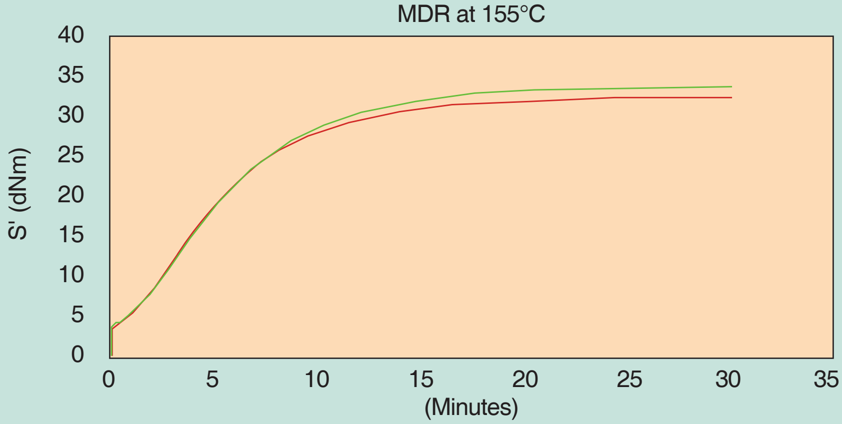
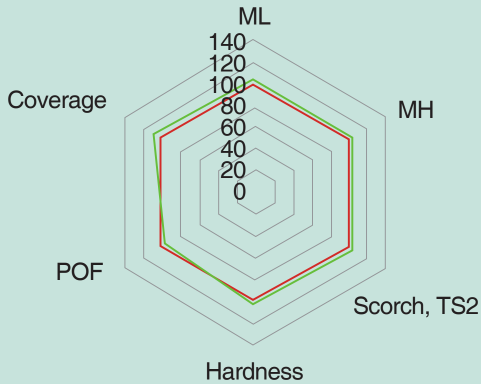


Figure 14 - performance comparison after vulcanizaton of these compounds, showing nearly identical performance for all tested items

LP 21-103 versus HMMM in a Re/Co formulation

Ingredients	*phr*	
Natural rubber	100	100
Carbon black N326	55	55
Palmera B 1805 pastillen	2	2
Silica (Evonik VN3)	15	15
TMQ	1	1
Petronas process oil N 100	4	4
ZnO red seal	6	5
Cobalt salt (ECOS S 9.3)	0.75	0.75
Resorcinol	3	3
HMMM powder	4.15	0
LP 21-103	0	6
Crystex-HD-OT-20	6	6
DCBS	0.6	0.6



ML: Minimum torque
MH: Maximum torque
TS2: Scorch time
POF: Pull out force
Coverage: Level of cord coverage

Non-aged values

RE/CO free low formaldehyde compound performance: TP 1862 + LP 21-103

Based on the positive results obtained with TP 1862 versus Re/Co, and LP 21-103 versus HMMM, additional testing was per-

Figure 15 - rheometer values for three different compounds as listed in the table, showing equivalent performance to the standard reference compound

Ingredients	*Reference Re/Co*	*TP 1862 + HMMM powder*	*TP 1862 + LP 21-103*
Natural rubber	100	100	100
Carbon black N326	55	55	55
Palmera B 1805 pastillen	2	2	2
Silica (Evonik VN3)	15	15	15
TMQ	1	1	1
Petronas process oil N 100	4	4	4
ZnO red seal	6	0	0
TP 1862	0	9.75	9.75
Cobalt salt (ECOS S 9.3)	0.75	0	0
Resorcinol	3	0	0
HMMM powder	4.15	4.15	0
LP 21-103	0	0	5.93
Crystex-HD-OT-20	6	6	6
DCBS	0.6	0.6	0.6
TBBS	0.9	0.9	0.9

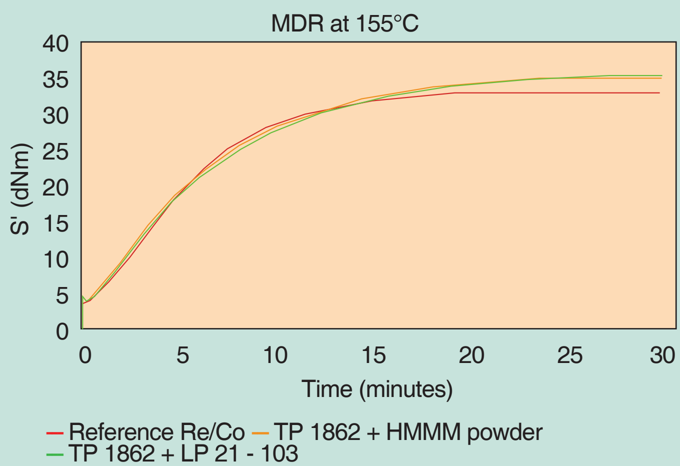
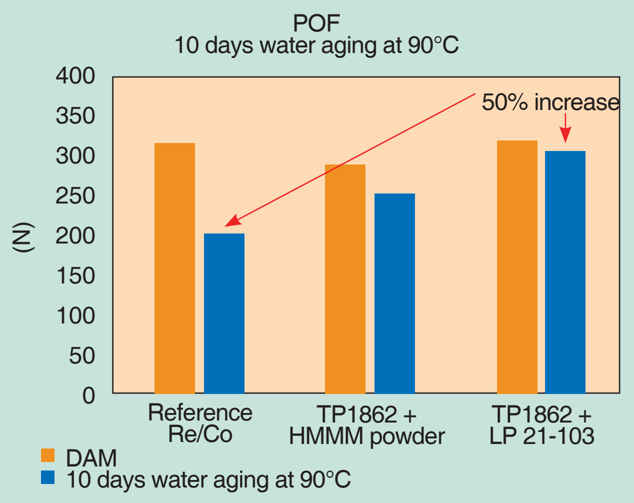


Figure 16 - synergistic benefit of using both TP 1862 and LP 21-103 versus a reference compound with Re/Co and HMMM POF when both are used



formed on rubber compounds using both additives. These results show substantial improvements in performance. Figure 15 shows rheometer values for three different compounds, as listed in the table, showing equivalent performance to the standard reference compound.

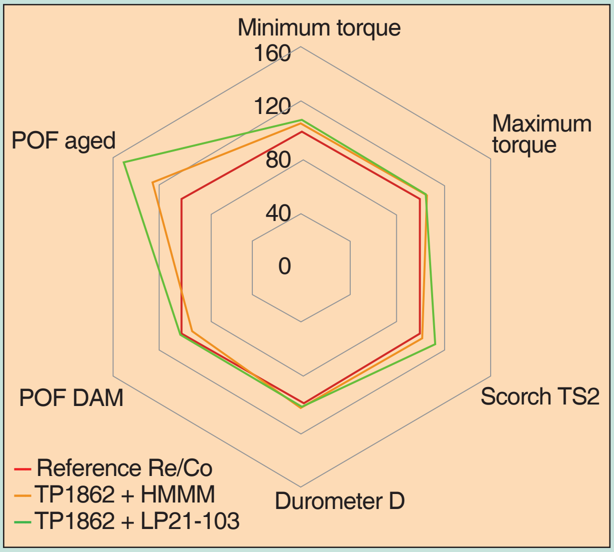
Figure 16 shows the synergistic benefit of using both TP 1862 and LP 21-103 versus a reference compound with Re/Co and HMMM. Note in particular a 50% increase in aged POF when both are used. Compound ingredient optimization is expected to reveal further benefits, such as reduced ingredient(s) levels for similar or slightly better performance as needed by the intended application.

Figure 17 shows additional performance attributes when these additives are combined, with equivalent or better performance for all parameters tested when compared to the reference compound. Further optimization of ingredient(s) levels are expected to reveal even better results.

Conclusions

Brüggemann's TP 1862 reactve extrusion additive is one solution for a sustainable way to eliminate Re/Co from rubber compounds. LP 21-103 can eliminate nearly all formaldehyde generated with HMMM during rubber processing, reducing human exposure and associated toxicity. Combining these additives

Figure 17 - additional performance attributes when additives are combined, with equivalent or better performance for all parameters tested when compared to the reference compound



shows significantly better performance than traditional compound recipes.

Further optimization with dosage in NR and other rubber types is ongoing and enables creation of better compounds with a more reliable supply chain. Brüggemann's rubber development laboratory is focused on new reactive extrusion rubber additives to improve compound performance, simplifiy processing and enhancing workplace safety.

This article is based on a paper presented at the 202nd Technical Meeting of the Rubber Division, ACS, October 2022.

References

1. ECHA link: https://echa.europa.eu/information-on-chemicals/evaluation/community-rolling-action-plan/corap-table/-/dislist/substance/100.003.260.

2. CIRS link: https://www.cirs-group.com/en/chemicals/the-european-commission-has-passed-the-resolution-on-adding-resorcinol-into-svhc-candidate-list.

3. OSHA.GOV link: https://www.osha.gov/formaldehyde/hazards#:~:text=Formaldehyde%20is%20classified%20as%20a,difficulty%2C%20eczema%2C%20and%20sensitization.