A tire manufacturing revolution
Superior adhesion of rubber, steel cord coated with Cu-Zn-Co ternary alloy
Purchasing tires with confidence - meeting regulations and methods to evaluate quality
Nonlinear models of mechanical properties reduce rubber recipe development time

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Superior adhesion of rubber and steel cord coated with Cu-Zn-Co ternary alloy

by Guy Buytaert, NV Bekaat SA, and Baoning Wang and Ywen Luo, Bekaat Asia

Steel cords are extensively used as a reinforcement material in radial tires, high pressure hydraulic hoses, rubber tracks and heavy duty conveyor belts. The use of steel cords leads to improved strength, stiffness, stability and uniformity in tires. Good adhesion between the rubber compound and the steel cord in the tire is critical to the tire’s performance. Not only will good adhesion ensure safe tire service under a variety of severe road and environmental conditions (e.g., moisture, salt water, etc.), it will also increase the tire’s lifetime. In order to guarantee a sufficient level of adhesion between the steel cord and rubber, the properties of both the metal surface and the rubber must be optimized. Therefore, Bekaat works continuously and in close cooperation with its customers to improve the adhesion between its steel cord and the customer’s rubber compound.

The brass coating (63.5% Cu and 36.5% Zn), electrolytically deposited on the steel surface, is the “bonding agent” that provides strong and robust adhesion between the reinforcing element (steel cord) and the adjacent rubber compound (adhesion or skin compound). Bonding between sulfur-cured rubber and steel cord occurs during the formation of an adhesion interface layer in the curing process. The adhesion build-up mechanism involves oxy-sulfidation reactions of sulfur species contained in the rubber compound with the Cu and Zn of the brass coating, forming a rough CuS layer at the interface, capable of physically bonding with rubber, as revealed by van Ooij (refs. 1 and 2).

In order to have good adhesion formation, and to reduce the rate of degradation of adhesion, particularly due to aging in hot and humid conditions, cobalt salts are added to the rubber (skin) compounds that are in contact with the steel cords. This has been the standard practice for over six decades (refs. 1-11).

However, these cobalt salts can be detrimental to the long-term properties of the cured rubber compound as a result of their pro-oxidant nature (ref. 9); hence, cobalt is considered to be a “poison” for rubber. Furthermore, cobalt salts added to rubber compounds can accelerate the rubber’s crack growth rate and lead to higher hysteresis in dynamic loading. Hence, the compounds can exhibit higher heat dissipation which can accelerate degeneration (aging) of the vulcanized rubber polymer and increase the tire’s rolling resistance (i.e., energy loss) (refs. 8-10). In addition, cobalt is an expensive, strategic material, and by adding cobalt randomly to the whole rubber compound, about 80% too much cobalt is used. It is estimated that only 20% of the cobalt adhesion promoting ingredients have a beneficial functionality at the brass surface.

Bekaert has introduced a breakthrough in tire reinforcement with TAWI (ternary alloy wire coating on tire cord). This patent-pending, new metallic coating for steel cord is comprised of copper, zinc and cobalt, and yields advancements in the performance and environmental impact of tires. TAWI uses cobalt where it is needed, at the interface between steel cord and rubber, eliminating the need for cobalt in the bulk rubber. Consequently, this innovative tire cord solution would strongly reduce the total amount of cobalt used in tires by 80-90%, which is extremely beneficial for the environment when the end-of-life usage of tires (recycling, etc.) (refs. 10 and 11) is considered. Moreover, the removal of cobalt salts as a rubber ingredient improves the ecological performance of tire manufacturing plants and enables healthier rubber compounding processes for tire workers. Furthermore, cobalt-free rubber compounds are more durable and exhibit less hysteresis. Together with significantly better adhesion in hot and humid conditions, TAWI spearheads the creation of longer-lasting and more eco-friendly passenger and truck tires. In figure 1, the most important expected benefits for TAWI reinforced, cobalt-free tires are plotted in a semi-quantitative manner.

Figure 1 - summary of the most important expected benefits for radial tires of usage of Cu-Zn-Co ternary coated steel cord (TAWI) in cobalt-free compounds compared to current standard brass coated steel cord in cobalt-containing adhesion compounds

![Figure 1 - summary of the most important expected benefits for radial tires of usage of Cu-Zn-Co ternary coated steel cord (TAWI) in cobalt-free compounds compared to current standard brass coated steel cord in cobalt-containing adhesion compounds](image-url)
steel cord. Also, the incorporation of cobalt inside the respective sulfide-oxide interfacial layers is highlighted. Incorporation of cobalt ions from the adjacent skin compound upon vulcanization was also shown by Fulton et al. (refs. 4-8), and it is claimed that doping of the semi-conducting Cu₄S-ZnS-ZnO interlayers by cobalt explains the slower dezincification of the underlying brass coating, which results in longer adhesion retention in hot and humid aging conditions. On the other hand, putting cobalt in the coating/interface, where its function is required, instead of in the rubber compound, appears to be the most efficient solution for optimal adhesion performance, with significantly better adhesion in hot and humid conditions. The cobalt incorporates more readily into the interfacial layers upon oxy-sulfidization of the coating metallic elements during compound vulcanization and adhesion build-up (ref. 10).

In this study, the adhesion performance of standard (63.5% Cu) brass-coated steel cord in a cobalt-containing skin compound is compared with a Cu-Zn-Co ternary alloy coated steel cord (with 67% Cu, 29% Zn and 4% Co) on a truck and bus radial (TBR) steel carcass cord in a cobalt-free compound. Specifically, the dynamic adhesion performance of the two adhesion systems is compared. Further, the dynamic mechanical properties ($E'$, $E''$ and tan δ) and crack growth rate with the DeMattia test) of both compounds are studied.

Table 1 - formulation (in phr) of the two compounds used in this study and the respective rheometer properties of the two compounds measured at 150°C, with (a) antioxidant, n-(1,3-dimethylbutyl)-n'-phenyl-p-phenylenediamine; (b) n,n-dicyclohexyl-2-benzothiazole sulfonamide; (c) n-tert-butyl-2-benzothiazole sulfonamide

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Compound with Co amount (phr)</th>
<th>Cobalt-free compound amount (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSR 10</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Carbon black N326</td>
<td>65</td>
<td>65</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>Manobond 680C</td>
<td>1.2</td>
<td>0.7</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1.8</td>
<td>1.8</td>
</tr>
<tr>
<td>6PPD (a)</td>
<td>0.8</td>
<td>0.7</td>
</tr>
<tr>
<td>DCBS (b)</td>
<td>6.4</td>
<td>6.4</td>
</tr>
<tr>
<td>TBBS (c)</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>Crystex HSOT20</td>
<td>1.8</td>
<td>3.5</td>
</tr>
<tr>
<td>Santogard PVI</td>
<td>12.0</td>
<td>13.0</td>
</tr>
<tr>
<td>Rheometer properties at 150°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tc2 (min.)</td>
<td>31.5</td>
<td>30.6</td>
</tr>
<tr>
<td>Tc90 (min.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MH (dN/m)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Experimental

The steel cord construction used in this investigation is 0.25 + 6 x 0.225 + 12 x 0.225 HT, with a brass coating of 63.5% Cu + 36.5% Zn, and a ternary alloy coating of 67% Cu + 29% Zn + 4% Co, both with a coating weight of 4.0 g/kg.

The formulations of the compounds used in this investigation are given in table 1, and are the same as in our previous study (ref. 10), in which their respective cure kinetics and mechanical properties were demonstrated. The removal of cobalt salts from the recipes slows down the cure kinetics. The most effective of the possible recipe modifications aims to restore the cure kinetics of the cobalt-containing original recipe by replacing, or partially replacing, DCBS by TBS1 or CBS. In order to achieve similar cure kinetics, such as Tc90, in the cobalt-free compounds, this “loss” is compensated for by replacing 0.8 phr DCBS with 0.7 phr TBS1 accelerator, by adding 0.7 phr stearic acid to the formulation to compensate for the “loss” of fatty acid from the cobalt carboxylic acid and adding 0.25 phr of retarder Santogard PVI to give more scorch safety to the compound.

The rheometer properties, as presented in table 1, were determined at 150°C with a Monsanto MDR 2000E moving die rheometer, provided by Alpha Technologies (ref. 10).

A crack growth propagation study of both compounds was done according to test standard ISO 132:2005, with 5 Hz test frequency, strain controlled amplitude and standard laboratory conditions (temperature and humidity as defined in ISO 23529).

Three test pieces, measuring 150 x 25 x 6.3 mm with an initial radius of 2.38 mm plus 2 mm initial crack length, were clamped into a Zwick DeMattia type of machine. The machine was started and stopped after specific intervals to measure the length of the cut.

Dynamic mechanical thermal analysis (DMTA, E', E'' and tan δ) of the two compounds was conducted with an Eplexor 100 N, applying a temperature sweep from -100°C to +100°C, 10 Hz and 2% dynamic deformation following ISO 4664-1:2005 (ref. 10). DMTA and DeMattia rubber fatigue testing was performed by Elastomer Research Testing B.V. (ERT) in Deventer, The Netherlands.

 Vulcanization of compounds and initial adhesion test samples were done, respectively, with an Agila cure press for adhesion testing and on a Fontaine cure press for DeMattia and DMTA compound testing in a dedicated test specimen mold for 25 minutes at 150°C.

The crosslink density of both cured compounds is defined in this study as the number of chain segments (between cross-links) per unit volume via a swelling method in line with ASTM D671-06 standard test methods for determining rubber properties. Approximately 1 g cured compound is put into a flask with 40 mL cyclohexane for 72 hours at 25°C; the sample is weighed immediately after being taken out from the solution; subsequently, the sample is heated at 70°C in vacuum conditions until the weight (m1) of the sample is stable. Based on the respective masses, the crosslink density of the cured compounds is calculated using the Flory formula:

$$V_c = \frac{1}{v} \left[ \ln \left( 1 - \frac{V_2}{V_1} \right) + V_2 \chi V_2^2 \right]$$

where:
- $V_c$ = cured compound crosslink density, mol/cm³;
- $V_2$ = volume fraction of polymer in the swollen polymer, %;
- $\chi$ = Flory-Huggins polymer-solvent interaction constant, here it is 0.44; and
- $v$ = molar volume of solvent, cm³/mol; (84.14/0.778 = 108.2)

$V_2$ is calculated as:

$$V_2 = \frac{V_1}{V_1 + V_{sc}}$$

$$V_{sc} = \frac{m_2 - m_1}{\rho_s}$$

where:
- $V_{sc}$ = solvent volume fraction in the swollen compound;
- $V_1$ = compound volume, $V_1 = m_1/\rho$;
- $\rho_s$ = solvent density, 0.778 g/cm³;
- $\rho$ = rubber density, 0.94 g/cm³;
- $f$ = rubber weight fraction in the compound, $f = 0.55$;
- $m_1$ = cured compound sample weight before swelling;
- $m_2$ = cured compound sample weight after swelling;
- $\rho_s$ = cured compound sample weight after heating weight.

Here, the dynamic adhesion performance of respectively coated steel cord and compounds is studied with an LDN-II cord dynamic sheath adhesion tester from the Rubber Info Company.

Figure 4 - picture of the cord dynamic sheath adhesion tester and pulling of steel cord out of rubber block according to ASTM D 2229
Table 2 - Dynamic mechanical properties of the two compounds used in this study, measured at 60°C, 10 Hz, 2% dynamic strain (ref. 10)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Compound with cobalt</th>
<th>Cobalt-free compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E'$ (MPa)</td>
<td>12.61</td>
<td>8.58</td>
</tr>
<tr>
<td>$E''$ (MPa)</td>
<td>1.98</td>
<td>0.94</td>
</tr>
<tr>
<td>Tan $\delta$</td>
<td>0.157</td>
<td>0.109</td>
</tr>
</tbody>
</table>

Figure 5 - POF (pull-out force, N) adhesion results of (a) brass-coated steel cord in Co-containing compound; (b) brass-coated steel cord in cobalt-free compound; and (c) Cu-Zn-Co ternary coated steel cord (TAWI) in cobalt-free compound upon RC (25 minutes cure at 150°C) and 24 hours steam aging at 105°C

(results 4) with test principles based on a DuPont de Nemours test from the 1960s (ref. 12). In this test, cords are vulcanized in a square-shaped rubber, measuring 12.5 x 12.5 mm, to form testing samples, and the two cord ends are fixed. During testing, six rubber samples are subjected concurrently to a reciprocating movement along the length of the cord with a certain amplitude and frequency at a pre-set temperature (ranging from room temperature to 100°C), and generating, thereby, a continuing dynamic shear at the interface between the cord and the rubber. With repeated shear deformation, the adhesion at the interface is gradually decreased in a given time period. After the given number of shear cycles, the sample is released from the dynamic tester and the remaining adhesion is measured. Using an Instron 5565 tensile tester, the force required to pull out the samples (POF [N]) is determined and the rubber coverage or appearance rating (APR [%]) is rated according to ASTM D 2229-02 (figure 4). Additionally, we introduced steam aging before applying dynamic loads. Samples were tested for 24 hours in a steam chamber heated to 105°C (after initial curing for 25 minutes at 150°C). Here, 160, 320 and 420 kilocycles were applied, with 40 N axial load, at room temperature, 13 Hz frequency and to 2 mm elongation.

Results and discussion

Compound properties

The main rheological properties at 150°C of the two compounds can be found in table 1. Te2 of the cobalt-free compound is a little higher, potentially due to the addition of the retarder, PVI. Te90 of both compounds is similar, which is an indication of the successful compensation for the elimination of cobalt salts from the compound. Maximum torque (MH), an indication of the crosslink density of the vulcanized compound, is a little lower for the cobalt-free compound, which also results in lower modulus of the cobalt-free compound (ref. 10). It is an indication that the increasing effect on crosslink density from the cobalt salt addition to a compound is not completely compensated for here. Increasing the concentration of sulfur and accelerator in the cobalt-free compound recipe is the most obvious way to increase MH, the crosslink density and, hence, the modulus of the compound. Another way to enhance the modulus is to increase the amount of carbon black added to the compound, but this might have the disadvantage of significantly increasing hysteresis. Adding to the cobalt-free compound, or increasing the level of resorcinol-HMNM (hexamethoxymethyl melamine) resin system, possibly with silica and TESP (bis-(triethoxysilyl)propyl) tetrasulfide)-silane, such as Si69, might positively affect the modulus without negatively affecting hysteresis. However, these modifications may slow down cure kinetics, and are also not perceived as making the compounding more safety-health-environmentally-friendly. Another way to improve cobalt-free compounds is to add secondary sources of crosslinking reactions, such as Duralink HTS or Perkalink 900 (refs. 9 and 13). Adding Perkalink 900 will further improve the reversion resistance and thermal stability of the compound, and adding Duralink HTS might lead to an improvement in fatigue and tear resistance (ref. 9).

A comparison of the dynamic crack propagation rate in both compounds, obtained according to DeMattia flex cracking principle, is plotted in figure 3. The cobalt-free compound has a lower crack growth rate; in particular, the difference between the two compounds grows with the increasing number of cycles. This result is completely in line with the earlier reported tear analyzer results (ref. 10), and is probably due to a longer network chain length or lower crosslink density.

Testing confirms that the compound with cobalt has a higher crosslink density (0.3504 mmol/cm² on average) than the compound without cobalt (average of 0.304 mmol/cm²); it is probably due to the function of the cobalt salt to accelerate the vulcanization speed and to give higher MH in rheometer and higher modulus of the compound (ref. 10).

In table 2, the dynamic mechanical properties of both compounds at 60°C, a temperature accepted as an indication for rolling resistance in the tire industry, are listed. The storage modulus $E''$, the loss modulus $E'''$ and tan $\delta$ of the cobalt-free
Table 3 - "RR relation" indicates which DMTA parameters are expected to contribute most to rolling resistance (RR); Δ DMTA (%) is the respective reduction in $E''$ and/or tan δ when going from a compound with cobalt to a cobalt-free compound; "RR (%) in tire" reflects the estimated portion this part (belt or carcass) of the tire contributes to RR; and Δ RR (%) is respective reduction in RR when going from a compound with cobalt to a cobalt-free compound.

<table>
<thead>
<tr>
<th>RR relation</th>
<th>Δ DMTA (%)</th>
<th>TBR RR (%)</th>
<th>PCR RR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Belt</td>
<td>Tan δ</td>
<td>-30.4 - 30.4</td>
<td>10.5 - 3.3</td>
</tr>
<tr>
<td>Carcass</td>
<td>$E''$ and tan δ</td>
<td>-52.5 - 52.5</td>
<td>3.5 - 1.5</td>
</tr>
<tr>
<td>Belt + carcass</td>
<td>$E''$ and tan δ</td>
<td>-52.5 - 52.5</td>
<td>13.5 - 4.7</td>
</tr>
</tbody>
</table>

Compound and Cu-Zn-Co ternary alloy coated steel cord in a cobalt-free compound upon initial adhesion (RC, regular cure) and after steam aging, after 0, 160, 320 and 420 cycles of cyclic loading, are shown. The appearance rating (APR) of the same samples was also judged because the combination of POF and APR makes a correct statement of the adhesion performance. In this study, the variations of the APR of the different coating and compound combinations upon dynamic loading or steam aging were not statistically significantly different.

Without dynamic loading, the level of the initial POF adhesion of the Cu-Zn-Co ternary alloy coating in a cobalt-free compound is about 10% lower than the reference system, whereas the initial APR adhesion of the different coatings in both compounds is similar and very good. After steam aging, without dynamic loading, the adhesion (retention) of the Cu-Zn-Co ternary alloy coating in the cobalt-free compound is the best, which is in line with our previous study (ref. 10). It can be explained by the low percentage of cobalt added to brass alloy that leads to a much slower dezincification than in normal brass, i.e., slower corrosion of the coating in hot and humid conditions and slower degradation of the adhesion interface.

Upon increasing the amount of cycles, without prior exposure to steam, a gradual decrease of POF can be observed in figure 5 for all three coating-compound combinations, yet the fastest drop in POF occurs for the brass coating in the cobalt-free compound. The cobalt-free compound was shown to have much better crack resistance (DeMattia results) which could make POF retain longer upon cyclic loading due to an "expected" slower fatigue degradation of the cobalt-free compound. However, a cobalt-free compound in combination with a brass coating is intrinsically known to be the weakest adhesion system, and that appears in this test to be the biggest driver, the sustained superior quality of the adhesion interface (i.e., Cu-ZnS-ZnO) under different demanding service conditions. The combination of steam aging and dynamic loading appears to lead to even more severe adhesion degradation. Also here, the Cu-Zn-Co ternary alloy coating in the cobalt-free compound is the best performing combination.

Conclusions
In this study, it has been shown that a Cu-Zn-Co ternary alloy coating, in combination with cobalt-free skin compounds, leads to several advantages:
- Improved adhesion retention in hot and humid conditions
- Improved adhesion retention in dynamic conditions
- Slower crack growth rate and improved heat resistance of skin compound
- Less hysteresis

Putting cobalt in the coating/interface, where its function is required, instead of in the rubber compound, appears to be the

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most efficient solution for optimal adhesion performance. Hence, a Cu-Zn-Co ternary alloy, with a low percentage of cobalt added to brass facilitates the removal of cobalt salts from the skin compounds in tires, and it can bring several benefits, such as longer lifetime of TBR tires. Less hysteresis indicates a potential reduction of rolling resistance of tires, which can lead to lower fuel consumption, less CO₂ and improved local air quality. Removal of cobalt salts as a compound ingredient also improves the ecological performance of tire plants and improves the working conditions of the tire workers.

References