Mixing Aspects of Sulfron 3001 in Carbon Black Compounds

Rubber · Carbon Black · Sulfron 3001 · Mixing temperature · Reaction temperature · Hysteresis characteristics

The mixing of Sulfron 3001 in carbon black compounds is described in this paper. The temperature-time profile of mixing between Sulfron and carbon black plays a critical role in realizing the positive effect of Sulfron on hysteresis characteristics. It has been shown that at a mixing temperature ≤ 140 °C, there is almost no reaction between carbon black and Sulfron 3001. On the other hand, temperature above 165 °C of mixing temperature, processing problems could occur because of side reactions of Sulfron 3001 on rubber. Two mixing sequences are described that provides the best results. It has been found that a temperature between 150-165 °C is required to get the reaction of Sulfron 3001 and carbon black started. The time plays an important role too. It is demonstrated that time required is about 2-2,5 minutes after Sulfron and carbon blacks are added to the rubber mixes after the desired temperature (150-165 °C) is reached.

Einmischen von Sulfron 3001 in rußgefüllte Mischungen

Kautschuk · Ruß · Sulfron 3001 · Mischungstemperatur · Reaktionstemperatur · Hystereseeigenschaften

Das Einmischen von Sulfron 3001 in rußgefüllte Compounds wird beschrieben. Um einen positiven Effekt von Sulfron auf die Hystereseeigenschaften zu erzielen wird der zeitabhängige Verlauf der Mischungstemperatur genutzt. Es wird gezeigt, dass bei Mischungstemperaturen von ≤ 140 °C keine Reaktion zwischen Ruß und Sulfron 3001 auftritt. Andererseits können bei Mischungstemperaturen oberhalb 165 °C durch Nebenreaktionen des Sulfron auch Verarbeitungsprobleme auftauchen. Es wurde gefunden , dass im Temperaturbereich von 150-165 °C die Reaktion zwischen Ruß und Sulfron startet, wobei die Reaktionszeit auch berücksichtigt werden muß. In einer Zeit von 2-2,5 min nach der Einarbeitung von Ruß und Sulfron und dem Erreichen der empfohlenen Temperatur wird die gewünschte Wirkung erzielt.

The tire industry is continuously striving to reduce the hysteresis of tire compounds. Lower hysteresis signifies lower heat generation translating into better durability and service life of tires. With the fuel price rising and concerns to improve the environment is growing, it is becoming important to reduce the rolling resistance of tire compounds. There are discussions on imparting future legislation regarding tire performance including rolling resistance and fuel economy [1].

A considerable reduction of rolling resistance is achieved in passenger tire section by exploiting green tire technology. In this technology, silica/silane concept is applied especially with modified synthetic rubber. For truck/bus tires, where today natural rubber is prime polymer, the use of silica/silane technology can not be applied. Teijin Aramid accepted this challenge and developed a new material based on Twaron that reduces the compound hysteresis significantly [2-26]. In this paper the mixing of Sulfron is described with an objective to realize the lowest hysteresis losses.

1 Composition of Sulfron 3001 in percentage

Component	Amounts, %
Twaron, PPTA	40
Stearyl stearate, Wax	30
Processing aid	20
Chemicals, reacted	10

2 Compound formulation

Compounds	1	2
SOG-10, NR	80	80
(Europrene)BR40	20	20
HAF- N326	53	53
Zinc oxide	5	5
Stearic acid	2	2
Non-Aromatic oil(NYTEX 840)	8	8
Santoflex 6PPD-pst	2	2
Flectol TMQ-pst	1	1
Sunolite 240 (Wax 240)	2	1,4
CBS-grs-2mm	1,5	1,5
Sulphur	1,5	1,5
Sulfron 3001		1,25
Total phr lab	176	176,65

* Lower amount of wax, because Sulfron contains Wax

Experimental

Compounds

Compounds were cured with CBS and sulphur. Zinc oxide, stearic acid, carbon black, oil, antidegradant were incorporated during the first stage Banbury mixing. Sulfron 3001, composition provided in Table 1, was also added in the Banbury during the non-productive stage. It is important that Sulfron 3001 should be added together with the carbon black. If technically it is not possible to add Sulfron together with the carbon black, it should be added as soon as possible just after addition of carbon black. See for more detail on mixing recommendation, section 3. The compound formulation is shown in Table 2.

Mixing

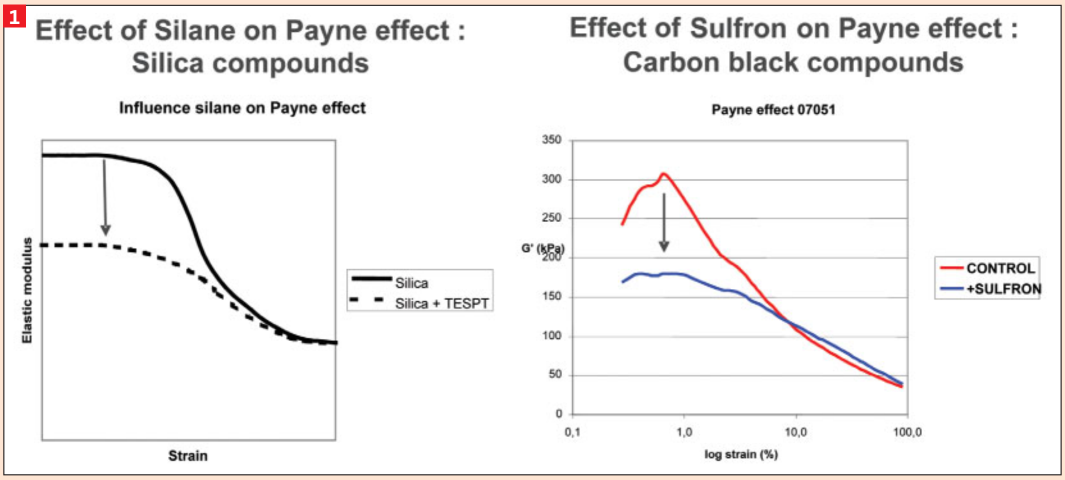
Master batches of the rubber formulation were prepared in a standard manner using a Banbury (1,6 L) using rotor speed of 76 rpm. The required amount of Sulfron 3001 was added to the mix on a Banbury allowing sufficient time and torque to disperse Sulfron into the rubber matrix. The curatives were added on a two-roll mill. The mixing sequence is shown in Table 3.

In order to achieve a temperature of 155-165 °C, higher rpm up to 145 rpm might be required. Please note that at 2½ minutes the rubber temperature should be > 150 °C.

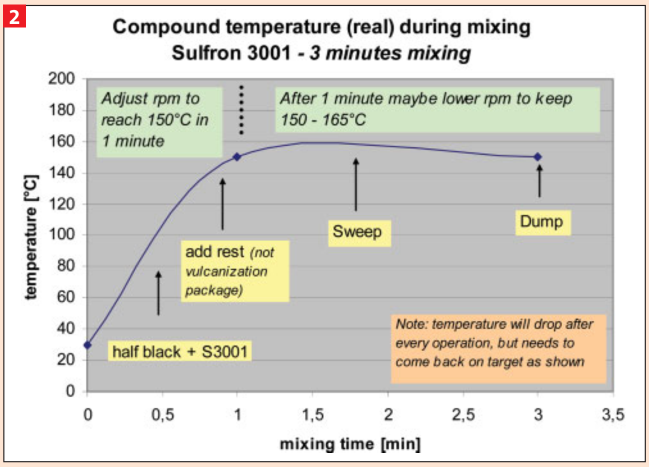
Authors

R. N. Datta, N. Huntink, M. van der Made, Arnhem (The Netherlands)

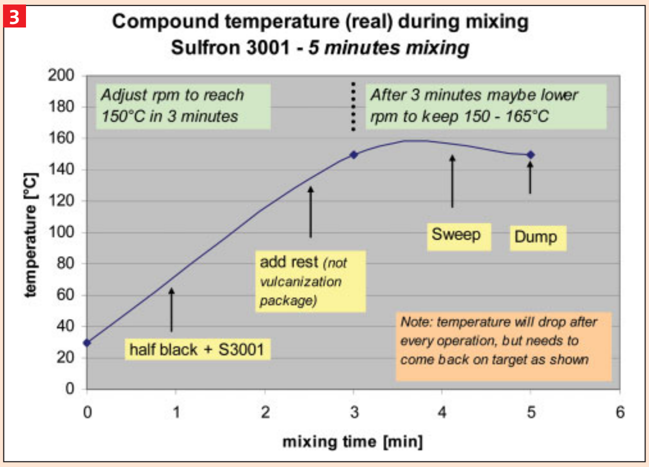
Corresponding author:
Rabin N. Datta
Teijin Aramid BV
Westervoortsedijk 73
6827 AV Arnhem, The Netherlands
E-mail:
Rabin.Datta@Teijinaramid.com



1 **Comparison of Payne effect of silica-silane versus carbon black-Sulfron 3001**



2 **Mixing time-temperature (Total mixing time: 3 min)**



3 **Mixing time-temperature (Total mixing time: 5 min)**

Payne effect measurement

The Payne effect of the compounds were studied by using a RPA 2000 (Alpha technologist, USA) at 100 °C and 0.5 Hz frequency at the dynamic strain amplitudes from a low strain of 0.7 % to a high strain of 100 %.

Hysteresis measurement

Viscoelastic properties were determined using a Gabo dynamic tester. Test conditions were 10 Hz and 60 °C with a dynamic strain of 2 % .

Results and discussion

Payne effect

Sulfron 3001 is a chemically modified Twaron matrix designed to react with filler, like carbon black. When added together with carbon black, it significantly decreases filler-filler interaction (Payne effect), reducing the frictional energy translated into lower hysteresis signifying reduction in rolling resistance and hence improving the fuel economy. An appropriate demonstration is shown in Figure 1.

Mixing recommendation

Carbon black and Sulfron 3001 are to be mixed together during the non-productive stage of mixing. Addition of Sulfron 3001 with polymer or in the final stage does not work as shown in earlier publication. Depending on the mixing time, mixing recommendation is shown in Figures 2 and 3.

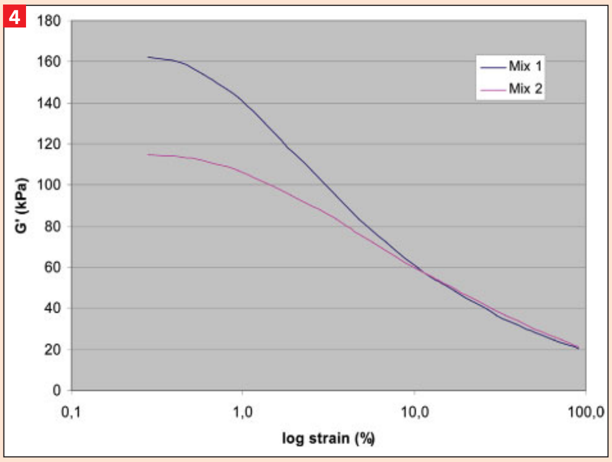
It is clear that Sulfron 3001 and carbon black are to be added as early as possible in the Banbury after the mastication stage of the polymer. The temperature should be raised to 150 °C by adjusting the rotor speed followed by the addition of rest of the ingredients (except curatives). The temperature (real) should be kept between 150-165 °C, and the mixing to be continued for atleast 2-2,5 minutes. A high starting temperature of the mixer (e.g. 90 °C) can also be chosen. The compounds (Table II) are mixed for 5 minutes according to the time-temperature protocol as shown in Figure 3. The Payne effect curves are plotted as shown in Figure 4.

3 **Mixing sequence**

Mixing procedure	Time, min
Elastomers	0
½ fller + Sulfron 3001	1
REST	2½
Sweep	4
Dump	5
Dump temperature	155-160 °C

4 **Hysteresis data.**

GABO const strain 60/10/2		CM / test piece / 1.5 t90 min. / 170 °C	
Compound		1	2
Temperature	[°C]	60	60
Frequency	[Hz]	10	10
Strain	[%]	2	2
Storage E'	[MPa]	5,001	4,603
Loss E''	[MPa]	0,7190	0,5074
Tan δ		0,1438	0,1102
Complex E*	[MPa]	5,052	4,631



4 **Payne effect of mixes 1 and 2**

The hystersis data are summarized in Table **4**.
It is clear from the data shown in Table 4 that Sulfron 3001 reduces the hysteresis significantly even with 1,25 phr of Sulfron 3001. Please note that E' is also reduced reflecting the lower Payne effect.

Effect of mixing temperature

Mixing at lower temperature (< 140 °C) or mixing at > 165 °C is not appropriate when Sulfron advantage is looked for. Below 140 °C (e.g. 120 °C), no or minimum reaction is expected to occur between carbon black and Sulfron 3001. At 165 °C, the processing problem pops up because of crosslinking involving side reactions. The mixing time and temperature effect is shown in Table **5**. The relative hysteresis data shows that the mixing is optimum when the temperature of mixing is between 150 °-165 °C.

Effect of mixing time and temperatures

The mixing time after carbon black + Sulfron 3001 is added plays an important role. As shown in the Table **6**, the hysteresis data decreases significantly when the dump temperature is > 150 °C < 165 °C and the mixing time after Sulfron and carbon black is added is at least 2,5 minutes. The effect of time of 1,5 minutes on tangent delta is less even if we increase the temperature to 160 °C.

Sequence of Sulfron 3001 addition

It is described earlier, the Sulfron 3001 only works if added together with carbon blacks. In order to analyse the effect, when Sulfron is added together with polymer or curatives at the final stage, several mixes were made with (1,5 phr Sulfron 3001) and without Sulfron 3001.

5 **Effect of maximum temperature during mixing**

	CONTROL	Sulfron 3001	Sulfron 3001	Sulfron 3001
Dump. Temperature, °C	150	150-165	120	>165
Hysteresis	100	70	95	Crosslinking

6 **Mixing time and temperature effect**

Mixing trial	A	B	C	D	E	F
Mixing time Sulfron [min.]	0	3,5	2,5	1,5	1,5	1,5
Dump temperature [°C]	150	150	150	150	155	160
Tan δ	0,128	0,098	0,105	0,117	0,109	0,109
Improvement [%]	Control	25	20	10	15	15

A= Control and B, C, D, E and F are with 1,5 phr of Sulfron 3001

7 **Payne effect**

Mixes	1	3	4	5
Sulfron addition	Control No Sulfron	Added together with carbon black	Added together with rubber	Added together with curatives
Payne effect	200	95	175	180

The Payne effect data are shown in Table **7**. It is clear from the Payne effect data that Sulfron 3001 only works when added together with Carbon black. The effect is negligible when Sulfron 3001 is added in the first stage together with polymer or at later stage together with curatives.

Applications

As Sulfron 3001 interacts with carbon black, the material is useful in all carbon black containing compounds. The application is not limited to tread but also could be used in body compounds, such as undertread, belt skim, carcass etc. It is important to indicate that the filler-filler interaction is reduced by applying Sulfron 3001. This is similar to silica/silane compounds where addition of silane reduces the silica-silica interaction (Payne effect).

Tread compounds

Tread compounds containing N-100 series or N-200 series, the application of Sulfron 3001 reduces the compound hysteresis by 15-20 %. This will be well reflected in the measurement where carbon-carbon interaction (Payne effect) is measured. Hysteresis (tangent delta) measured at 60-70 °C at 10-15 Hz with 1-2 % DSA shows a decrease of 15-20 %. More studies are now carried out to nail down the effect of time/temperature of mixing.

Undertread or belt compounds

Generally undertread compounds or belt skim compounds are reinforced with N-300 series of black. With N-326 black, the effect of Sulfron 3001 (2 phr) shows a reduction of tangent delta with more than 30 %. This is a remarkable achievement based on tire compounds requirements.

Guidelines

- Please follow the mixing time-temperature profile
- Add Sulfron 3001 together with carbon black or as early as possible after addition of carbon blacks.
- Avoid using peptizers because it can disturb the reaction. Sulfron 3001 reduces compound viscosity and so elimination of peptizer can bring positive results in properties.
- In Silica compounds, please add Sulfron 3001 after silica/silane reaction is completed.
- In mixed filler package, please add Sulfron 3001 after silica/silane reaction is completed.
- Fill factor of 70 % is advised (can be optimized based on viscosity).

Conclusions

As described, Sulfron 3001 reacts with carbon black, it is vital therefore that the mixing is properly done. As a recommendation, the following should be taken care:

- Sulfron 3001 should be mixed in Banbury mixers together with carbon black
- Sulfron 3001 does not work when mixed together with the polymer
- Sulfron 3001 does not work when mixed with the curatives

The mixing time and temperature is critical. Time plays a more important role than temperature. It is suggested that a mixing time of at least 2,5 minutes is required to obtain the required properties. The dump temperature (real rubber temperature) should lie between 150-165 °C (maximum).

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