

Use of 1,3-bis(citraconimidomethyl)benzene as an antireversion agent in industrial rubber products

R.N. Datta and F.A.A. Ingham

Flexys, Deventer (NL)

Selected from *International Polymer Science and Technology*, 29, No. 6, 2002, reference GK 02/04/225; transl. serial no. 14778

Translation submitted by C. Hinchliffe

The following article describes the use of an antireversion agent which is useful for various applications of rubber products.

1,3-bis(citraconimidomethyl)benzene was evaluated in a series of typical applications in industrial rubber products and demonstrated advantages with regard to reversion resistance, during curing and following ageing. This improvement to the reversion resistance results in a better retention of vulcanisate properties such as tensile strength, crack growth resistance and abrasion resistance. In addition, heat evolution is significantly reduced in the presence of an anti-reversion agent.

1. INTRODUCTION

1,3-bis(citraconimidomethyl)benzene, Perkalink 900 (Figure 1), is a unique chemical compound which protects sulfur-cured mixtures against the impacts of reversion, the thermal destruction of sulfur crosslinks. The reversion process results in a decrease in the crosslink density and hence a reduction in the physical properties of the vulcanisates [1]. In practice, reversion may occur during vulcanisation and/or during the service life of the vulcanised rubber product.

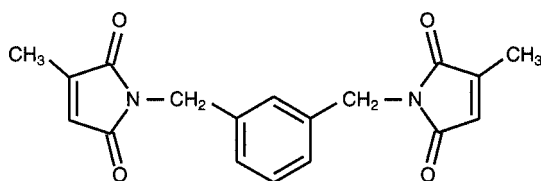


Figure 1 Antireversion agent 1,3-bis(citraconimido-methyl benzene)

During the vulcanisation of thick-walled products, for example, the mixture is exposed to vulcanisation periods at and close to the surface which extend way beyond the optimum for vulcanisation. This is unavoidable due to the time required to ensure sufficient vulcanisation in the interior of the product. A similar situation may occur with the vulcanisation of smaller products if an attempt is made to increase productivity by using higher vulcanisation temperatures.

Reversion may also occur during the service life of a product if it is subjected to dynamic stress at high temperatures. This process keeps going since the reduction in the physical properties results in increased heat evolution, which in turn accelerates the reversion process. The result is a loss of dynamic properties, a reduced service life and under some circumstances a catastrophic failure [2]. The common method for combating the harmful effects of reversion is concentrated on the use of SEV (semi-efficient) or EV (efficient) vulcanisation systems [3]. These vulcanisation systems work with a high accelerator : sulfur ratio or sulfur donors to reduce the formation of polysulfidic crosslinks. Reversion resistance is improved since the network formed is based on di- and monosulfidic crosslinks with better thermal stability. However, this improvement in reversion resistance is achieved at the cost of a reduction in scorch resistance, fatigue resistance and other properties linked to strength.

In an ideal case, a system to combat reversion should not impair the desired material properties, but should ensure that they are retained under conditions which would otherwise result in their reversal. In addition, the mixture's scorch time and the vulcanising rate should not be impaired.

1,3-bis(citraconimidomethyl)benzene counteracts reversion in a new way: by means of crosslink compensation [4-8]. Immediately after the onset of reversion, it generates thermally stable crosslinks based on C-C bonds and thereby compensates the loss of thermally unstable polysulfidic crosslinks. As a result, the crosslink density and material properties are retained after the onset of reversion. At the same time, the scorch time and vulcanisation rate are unaffected since the *chemical* remains inactive before reversion takes place. In practice, therefore, the material may be added to the mixture from the start without any further changes to the formulation or processing conditions being required.

Studies into the model mechanism [9, 10] have shown that the antireversion agent compensates the loss of polysulfidic crosslinks by reacting with the conjugated diene and triene structures formed along the polymer chain during reversion and hence generates new crosslinks. A schematic diagram of the mechanism is shown in **Figure 2**. The formation of these crosslinks takes place by means of a double Diels-Alder reaction (**Figure 3**).

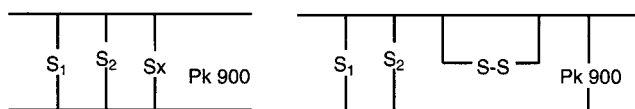


Figure 2 Schematic diagram of the antireversion mechanism

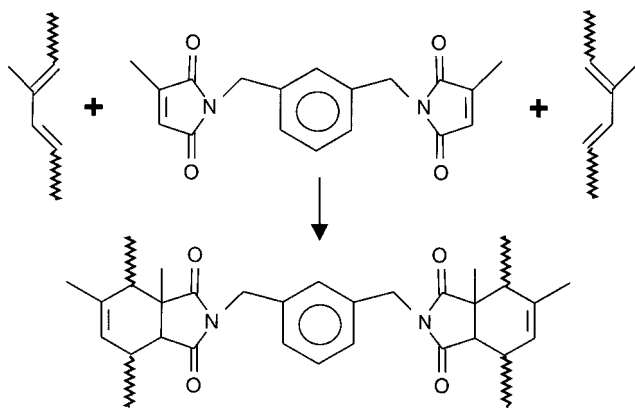


Figure 3 Diels-Alder reaction

In addition to the formation of these new thermally stable crosslinks, the unsaturated diene and triene groups are removed and this again has an advantageous impact on the physical properties of the vulcanisates [11].

In view of the mechanism described, it is evident that the antireversion agent is more effective in vulcanisates with a high content of polysulfidic crosslinks since these readily undergo reversion resulting in the formation of conjugated diene and triene structures. This means that the vulcanisation system's sulfur-accelerant ratio is to a large extent the decisive factor regarding the suitable concentration of antireversion agents.

2. DOSES

Table 1 contains a list of recommended doses; these should be seen as starting values for trials. Doses higher than these may result in excessive moduli in the case of overcuring or during the use of the product. This could have negative impacts on vulcanisation properties such as tear propagation resistance and dynamic fatigue resistance. A rheometer curve can serve as a useful reference for the optimum dose: here, a dose resulting in a vulcanisation plateau is desirable, while, on the other hand a "marching modulus" curve is not desirable. In between, for example vulcanisation systems between SEV ("semi efficient") and CV ("conventional") systems should receive additives in suitably selected intermediate doses.

Polymer system	Vulcanisation system	Perkalink 900, phr
NR, IR and blends	EV	0.25
With < 50 % SBR or BR	SEV	0.50
	CV high S-dose	0.75
SBR, BR, NBR	SEV CV	0.25 0.50

3. PREPARING AND PROCESSING THE MIXTURE

Perkalink 900 is stable at conventional mixing and processing temperatures for rubber. The material undergoes thermal decomposition at 240 °C and melts at 90 °C and hence its dispersion should not present any problems when mixed in an internal mixer. However, it is recommended that the chemical be added in a multi-stage mixing process during the premixing stage to achieve the best possible dispersion. The Perkalink 900 has no impacts on a mixture's scorch behaviour or vulcanisation rate and hence the mixtures may be processed in the normal way. The chemical may be added to existing mixtures without any further changes to the mixture being necessary. It may be the case that mixing on an open roll mill does not result in optimum dispersion if the mixing temperature is below 90 °C. To facilitate dispersion, the chemical should also be added on the roll in the first stages of the preparation of the mixture.

3.1 Laboratory tests

When testing mixtures containing Perkalink 900, the test conditions should correspond to the conditions of use, particularly if there is overcuring. Perkalink 900 *only* acts immediately after the onset of reversion and consequently there is no advantage to the mechanical properties formed during optimum vulcanisation. On the other

hand, one of the more striking features of Perkalink 900 is its inactivity at the start of the *normal*, which causes the target properties of the optimum-crosslinked vulcanisate to be retained *unchanged*. In order to be able to determine the advantageous impacts of Perkalink 900, test and ageing conditions simulating reversion should be selected in which vulcanisation in the mould and/or during the *planned use* may be expected. In particular, measurements of the heat evolution should be taken on a Goodrich flexometer over a long period at a temperature such as those expected during use. Overcompensation of the loss of polysulfidic crosslinks due to the addition of an excessive amount of the chemical results in a "marching modulus" curve and during ageing there may be a significant increase in the modulus. It is, therefore, recommended that the stress-strain properties after ageing be incorporated in the test program.

3.2 Applications

The most important fields of application of antireversion agents are found in the tyre industry, in particular for heavy-duty tyres where a high content of natural rubber is used. Here, the advantage is during vulcanisation and during subsequent use when high temperatures often develop. However, fields of application outside the tyre industry may also benefit from *this usage*, during the vulcanisation process and during the product's service life. The chemical is in particular able to prevent reversion during the vulcanisation process if high temperatures are used to increase productivity as a result of reduced heating times. **Table 2** lists some of the products for which the use of Perkalink 900 could be advantageous.

Application	Polymer
Conveyor belt cover plate	NR
Engine mounting	NR
Tank pressure rest	NR/SBR/BR blend
Oil seal	NBR

4. RESULTS AND DISCUSSION

4.1 Conveyor belt coatings – NR

The most important characteristics for the determination of the properties of conveyor belts in particular conveyor belt coatings are: dynamic fatigue resistance, abrasion resistance and low heat evolution. The effect of 1,3-bis(citraconimidomethyl)benzene on these key properties was tested in addition to the vulcanisation behaviour and

the tensile-stress properties in a typical formulation for a conveyor belt covering based on NR (**Table 3**).

Compound ingredients	Reference variants	Perkalink 900
NR	100	100
N330	45	45
Aromatic oil	4	4
ZnO	5	5
Stearic acid	2	2
6PPD	1	1
CBS	0.5	0.5
Sulfur	2.5	2.5
Perkalink 900	-	1

The vulcanisation behaviour is shown in **Figure 4**. The antireversion agent has no impact on the scorch resistance and the optimum vulcanisation time. The beneficial effect is evident, if reversion sets in, as observed with the reference mixture. In contrast, the mixture containing the antireversion agent retains a torque value close to the maximum.

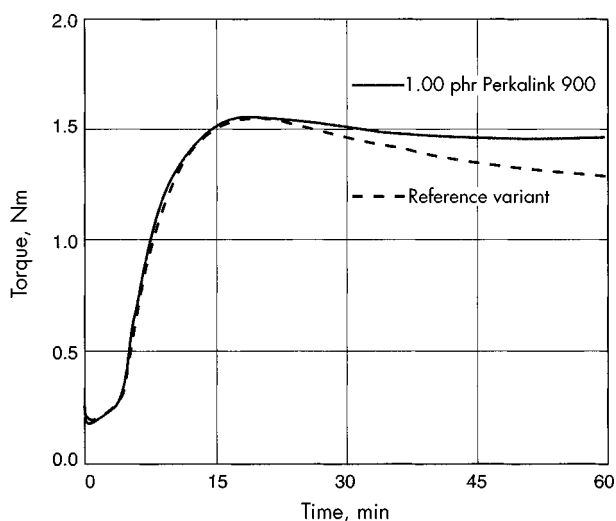


Figure 4 Vulcanisation behaviour at 150 °C

The antireversion impact is also expressed in the stability of the vulcanisation properties after overcuring or heat ageing in the air at 100 °C. The values for tensile stress, crack propagation in the folding endurance test and abrasion resistance are much better in the material containing the antireversion agent (**Figures 5, 6 and 7**).

One important advantage relates to the heat evolution under dynamic conditions of use, such as those encountered during the use of conveyor belts. Both during optimum

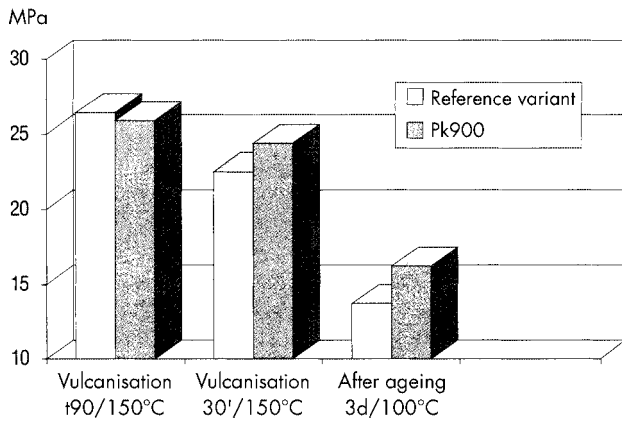


Figure 5 Tensile strength

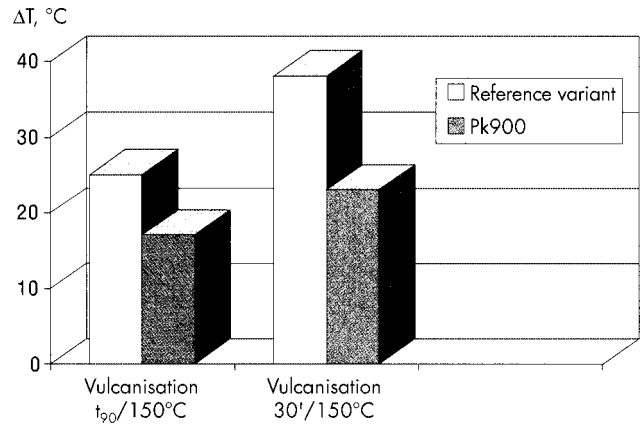


Figure 8 Heat evolution after 30 minutes testing on the Goodrich flexometer at 100 °C ambient temperature (stress 108 N, amplitude 4.45 m, frequency 30 Hz)

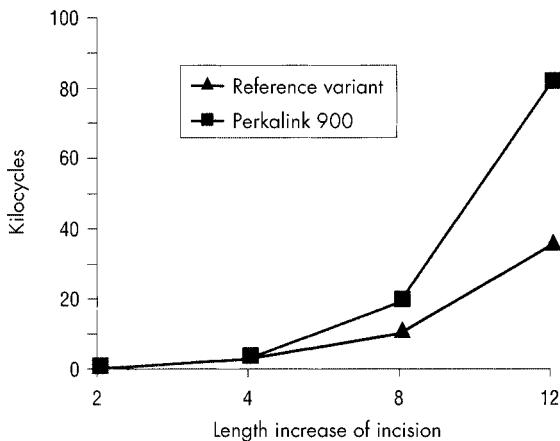


Figure 6 DeMattia crack propagation: samples vulcanised for 30 minutes at 150 °C

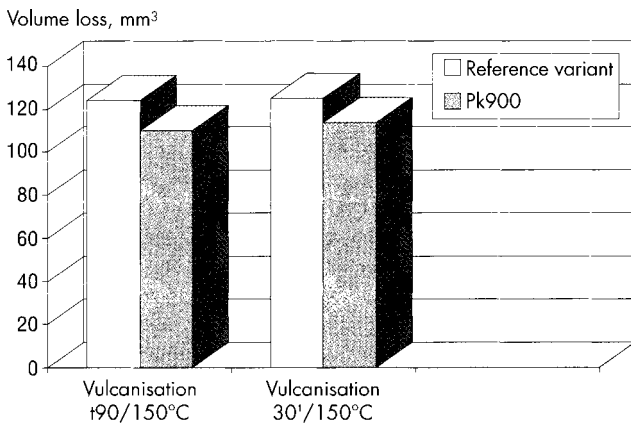


Figure 7 Abrasion loss according to DIN

vulcanisation and overcuring, the antireversion agent is extraordinarily effective for reducing heat evolution as determined during tests on the Goodrich flexometer (Figure 8). The reference material, which did not contain any antireversion agent had a much higher heat evolution. This indicates that the rolling losses may be reduced by the use of Perkalink 900.

4.2 Engine mounting – NR

The most important properties of an engine mounting are low heat evolution and low compression set under dynamic stress. These properties were determined for a typical material for an engine bearing based on NR with and without Perkalink 900 (Table 4).

Compound ingredients	Reference variants	Perkalink 900
NR	100	100
N-660	42	42
Zinc oxide	5	5
Stearic acid	2	2
Oil	9	9
MC wax	2	2
δPPD	2	2
TMQ	2	2
Resin	2	2
Santocure CBS	1.5	1.5
Perkazit TMTD	0.2	0.2
Sulfur	2.25	2.25
Perkalink 900	-	0.75

Unlike the preceding example, the formulation for the engine mounting contains a vulcanisation system which tends towards an SEV system; compared to a CV vulcanisation system this should already provide a high degree of reversion resistance. Nevertheless, the antireversion agent can still give rise to a significant additional effect.

The vulcanisation parameters show that Perkalink 900 has no impact on the scorch time or the optimum vulcanisation time (Table 5). The values for tensile strength

	Reference variants	Perkalink 900
ML, N x m	0.17 (0.16)	0.16 (0.15)
MH-ML, N x m	1.49 (1.35)	1.43 (1.34)
t_{s2} , min	4.1 (1.1)	4.1 (1.1)
t_{90} , min	8.7 (2.5)	8.4 (2.4)
Scorch time t_5 (121 °C)	25.6	25.4

in overcured condition (at 150 °C and 170 °C) and after ageing at 100 °C also point to a trend towards better strength properties (Figure 9).

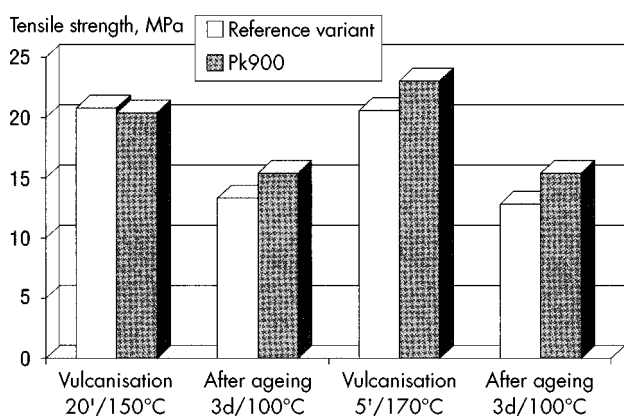


Figure 9 Tensile strength

The important vulcanisation properties required for this type of application, i.e. low heat evolution and low permanent deformation after dynamic stress was determined by testing on a Goodrich flexometer. The vulcanisate with antireversion protection revealed a clear decrease in the heat development and the permanent deformation after dynamic stress (Figures 10 and 11).

Even at the high vulcanisation temperature of 170 °C, after dynamic stress, there was little change in the heat evolution and permanent deformation of the material with Perkalink 900 compared to the material vulcanised at a lower temperature. On the other hand, at the higher vulcanisation temperature, the reference material underwent both increased heat evolution and increased permanent deformation after dynamic stress. This points to the conclusion that in this case an increase in the vulcanisation temperature with the aim of increasing productivity has no disadvantageous impacts on the performance of the vulcanisate.

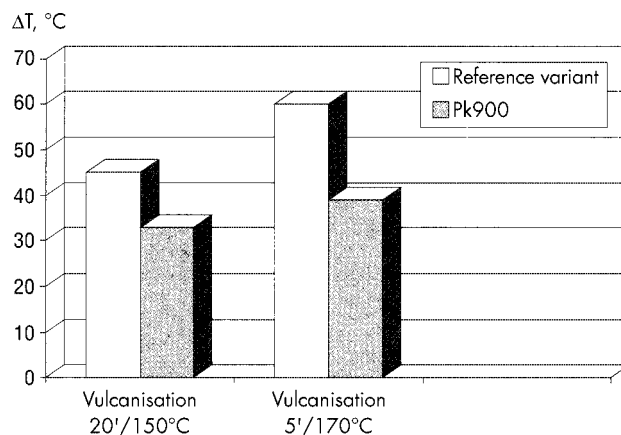


Figure 10 Heat evolution after 30 minutes testing on the Goodrich flexometer at 100 °C ambient temperature (stress 108 N, amplitude 4.45 mm, frequency 30 Hz)

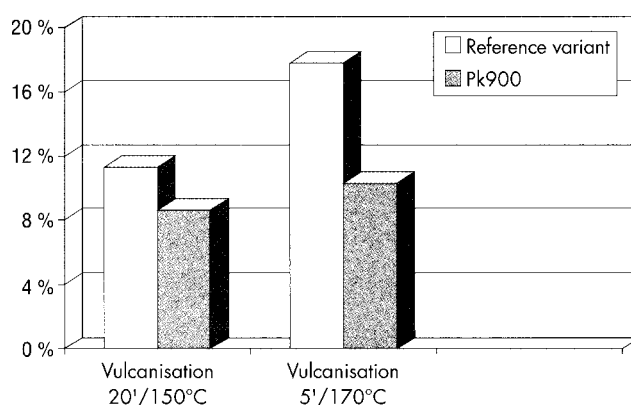


Figure 11 Permanent deformation after 30 minutes testing on the Goodrich flexometer at 100 °C ambient temperature (stress 108 N, amplitude 4.45 mm, frequency 30 Hz)

4.3 Tank container pressure, NR/SBR/BR blend

Perkalink 900 is also effective in mixtures based on blends of NR and SBR/BR. Tests with a formulation for a tank container pressure rest produced evidence that heat evolution is reduced with dynamic stress in an overcured condition. Overcuring is a general problem with the production of the relatively thick-walled products. The formulations for one reference and two test mixtures, in which two different amounts of the antireversion agent were tested are given in Table 6. The associated vulcanisation parameters are listed in Table 7.

While hardly any advantages may be determined with regard to the physical properties of the vulcanisates (Table 8), there is an advantage in the form of lower heat evolution under dynamic stress (Figure 12). In addition, the antireversion agent endows a higher wear resistance (Figure 13). This finding is of great practical significance as it is not unusual for tank container pressure rests to fail due to wear during use.

Mix components	1	2	3
NR	60	60	60
SBR 1500	20	20	20
BR Buna CB 10	20	20	20
Carbon black N220	70	70	70
Zinc oxide	4	4	4
Stearic acid	2	2	2
Oil	40	40	40
Santoflex 6PPD	1	1	1
MC wax	3	3	3
Santocure TBBS	1	1	1
Perkazit MBTS	2	2	2
Santogard PVI	0.15	0.15	0.15
Sulfur	2	2	2
Perkalink	-	0.5	0.75

	1	2	3
ML, N-m	0.18	0.18	0.18
MH-ML, N-m	1.37	1.33	1.31
ts ₂ , min	3.4	3.6	3.7
t ₉₀ , min	7.2	7.3	7.3

Properties	1	2	3
Modulus 300 %, MPa	9.9	9.9	9.9
Tensile strength, MPa	17.4	17.8	18.0
Elongation at break, %	475	470	470
Tear propagation resistance, kN/m	67	75	72
Abrasion loss, mm ³	88	75	72

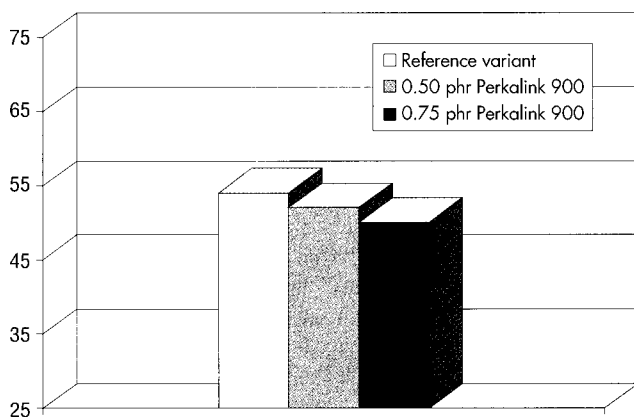


Figure 12 Heat evolution after 60 min test on the Goodrich flexometer at 100 °C ambient temperature (load 108 N, amplitude 4.45 m, frequency 30 Hz)

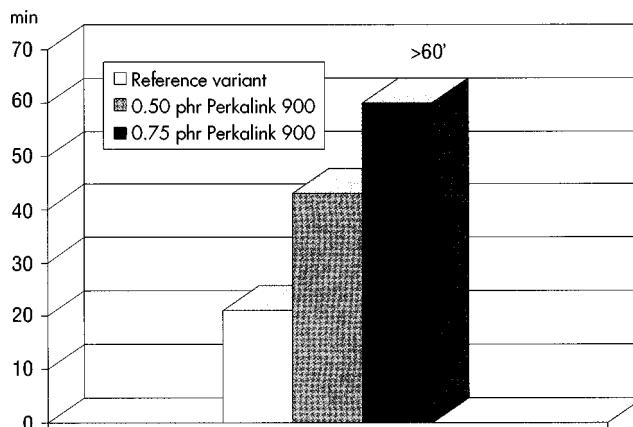


Figure 13 Fatigue time with test on the Goodrich flexometer at 100 °C ambient temperature (blow out; load 216 N, amplitude 4.45 m, frequency 30 Hz, max. test duration 60 min)

4.4 Oil seal – NBR

Perkalink 900 has been tested in the formulation for an oil seal based on NBR, in which the most important properties are compression set and oil resistance. The test formulations are listed in **Table 9** and the vulcanisation parameters in **Table 10**.

Mix components	Reference variant	Perkalink 900
NBR	100	100
Carbon black N-550	60	60
ZnO	5	5
Stearic acid	1	1
DOP	15	15
TMQ	2	2
MBTS	1	1
TMTD	0.1	0.1
Sulfur	1.5	1.5
Perkalink 900	1.5	0.75

	Reference variant	Perkalink 900
ML, N-m	1.36	1.39
ts ₂ , min	0.9	0.9
t ₉₀ , min	1.9	2.1

With greatly extended overcuring, which may be considered to be an anaerobic ageing process, material containing an antireversion agent has increased tensile strength and increased values for other physical properties, as shown in **Table 11**.

Properties	Reference variant	Perkalink 900
Modulus 300 %, MPa	12.9 (13.6)	13.3 (14.0)
Tensile strength, MPa	19.0 (18.2)	20.4 (21.1)
Elongation at break, %	530 (470)	560 (470)
Tear propagation resistance, kN/m	62 (55)	65 (60)

Both the residual deformation after dynamic stress and the resistance to swelling in oil are improved by the addition of Perkalink 900, which is an indication of the greater thermal and mechanochemical resistance of the crosslinks formed by Perkalink 900. The relevant data are shown in **Figures 14 and 15**.

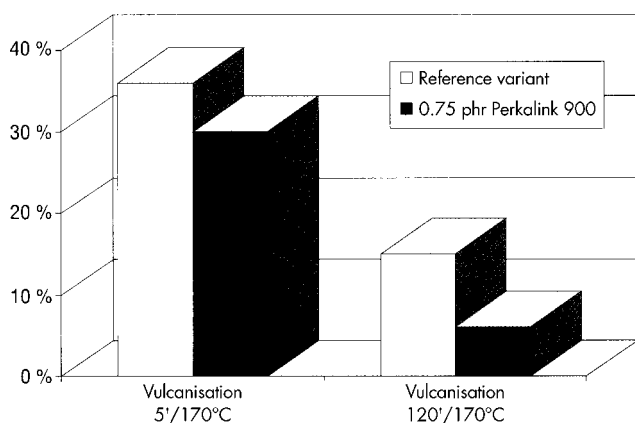


Figure 14 Residual deformation after 120 min. test on the Goodrich flexometer at 100 °C ambient temperature (load 108 N, amplitude 4.45 m, frequency 30 Hz)

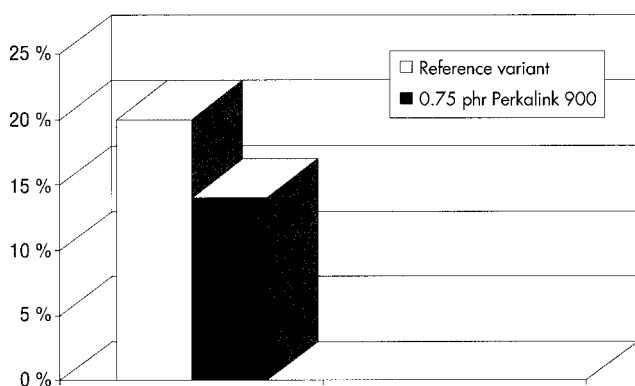


Figure 15 Swelling in ASTM oil No. 3, 168 h at 150 °C - samples cured for 5 mins at 170 °C

Apart from the formulations investigated, there are possible further applications with the following products:

- bridge bearings
- pneumatic springs
- silent bushings
- ships' fenders
- rolls
- bases for roll mills
- membranes
- O-rings
- bellows
- heating bladders for vulcanising presses

REFERENCES

1. J.I. Cunneen and R.M. Russel: J. Rubber Res. Inst. Malaysia 22 (3), 300, 1969
2. A.I. Medalia, Rubber Chem. Technol., 64, 481, 1990
3. T.D. Skinner and A.A. Watson, Rubber Age, 99, 76, 1967
4. R.N. Datta, J.H. Wilbrink and F.A.A. Ingham, India Rubber J. 8, 52, 1994
5. R.N. Datta and M.S. Ivany, Rubber World 212 (5), 24, 1995
6. R.N. Datta and W.F. Helt, Rubber World 216 (5), 24, 1997
7. R.N. Datta and J.C. Wagenmakers, Kautschuk Gummi Kunststoffe, 49, 671, 1996
8. R.N. Datta, A.G. Talma, J.C. Wagenmakers and D. Seeberger, Gummi Fasern Kunststoffe, 49, 892, 1996
9. A.H. Schotman, P.J.C. van Haeren, A.J.M. Weber, F.G.H. van Wijk, J.W. Hofstraat, A.G. Talma, A. Steenbergen and R.N. Datta: Rubber Chem. Technol. 69, 727, 1996
10. R.N. Datta et al.: Rubber Chem. Technol. 70, 129, 1997
11. R.N. Datta and J.C. Wagenmakers: J. Polym. Materials, 15, 379, 1998

(No date given)