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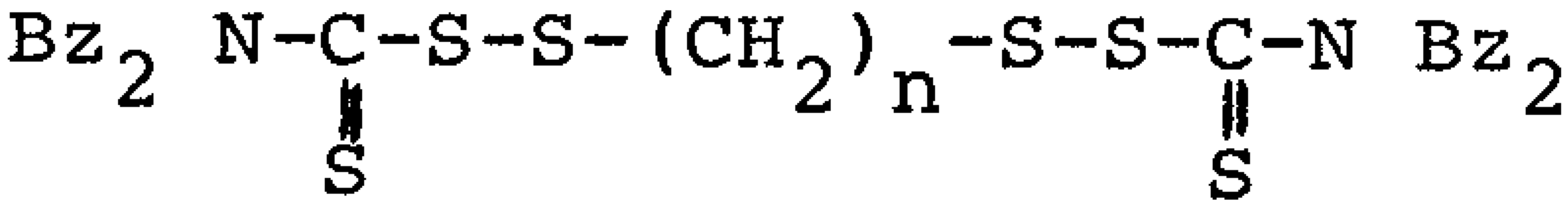
(72) Inventeurs/Inventors:
Nordsiek, Karl-Heinz, DE;
Zerpner, Dieter, DE;
Wolpers, Jürgen, DE
(73) Propriétaire/Owner:
BAYER AKTIENGESELLSCHAFT, DE
(74) Agent: FETHERSTONHAUGH & CO.

(54) Titre : PROCEDE POUR LA PREPARATION DE VULCANISATS DE CAOUTCHOUC DIENIQUE
(54) Title: PROCESS FOR THE PREPARATION OF DIENE RUBBER VULCANISATES



$$Bz_2N-\underset{\underset{S}{\|}}{C}-S-S-(CH_2)_n-S-S-\underset{\underset{S}{\|}}{C}-NBz_2$$

(57) Abrégé/Abstract:

A process for the preparation of diene rubber vulcanisates is disclosed. The vulcanisation is carried out at temperatures from 140 to 200°C, in the presence of 1 to 4.5 parts per 100 parts of rubber of crosslinker substances of the formula (see above formula) wherein n is 2 or 6 and Bz is benzyl, in the presence of a very small quantity of sulphur and a small quantity of a mercapto accelerator, a sulphenamide accelerator or a mixture thereof. The process of the invention produces elastomers having an outstanding ageing stability and reversion stability after a relatively short vulcanisation time using economical amounts of crosslinker substances and avoiding blooming phenomena in the vulcanisate.

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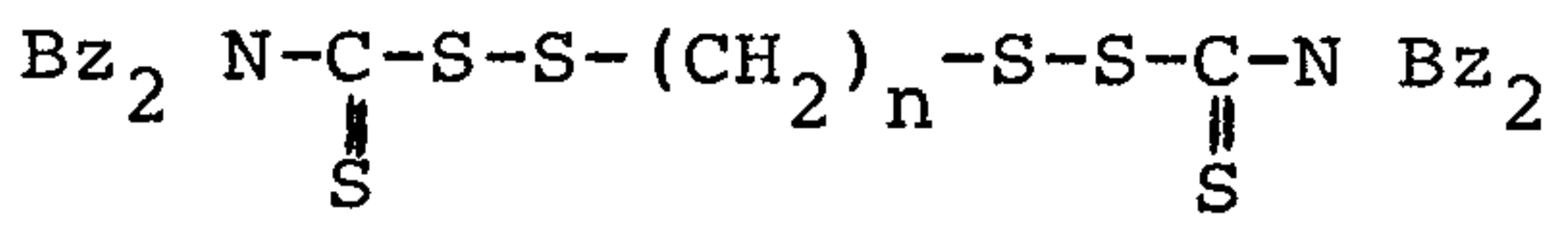
ABSTRACT

A process for the preparation of diene rubber vulcanisates is disclosed. The vulcanisation is carried out at temperatures from 140 to 200°C, in the presence of 1 to 4.5 parts per 100 parts of rubber of crosslinker substances of the formula



$$Bz_2\,N-\underset{\underset{S}{\|}}{C}-S-S-(CH_2)_n-S-S-\underset{\underset{S}{\|}}{C}-N\,Bz_2$$

wherein n is 2 or 6 and Bz is benzyl, in the presence of a very small quantity of sulphur and a small quantity of a mercapto accelerator, a sulphenamide accelerator or a mixture thereof. The process of the invention produces elastomers having an outstanding ageing stability and reversion stability after a relatively short vulcanisation time using economical amounts of crosslinker substances and avoiding blooming phenomena in the vulcanisate.

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Patentabteilung

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Process for the preparation of diene rubber vulcanisates

Diene rubbers are amongst the most frequently used all-purpose rubbers. These are understood as meaning polymers and copolymers of butadiene, styrene and also isoprene. Natural rubber and synthetic polyisoprene are also to be regarded as diene rubbers. These rubbers are inexpensive and available in large amounts and have good general properties. A disadvantage of this group of rubbers is a structure-related, only limited to inadequate aerobic and anaerobic ageing resistance and heat stability of their sulphur vulcanisates.

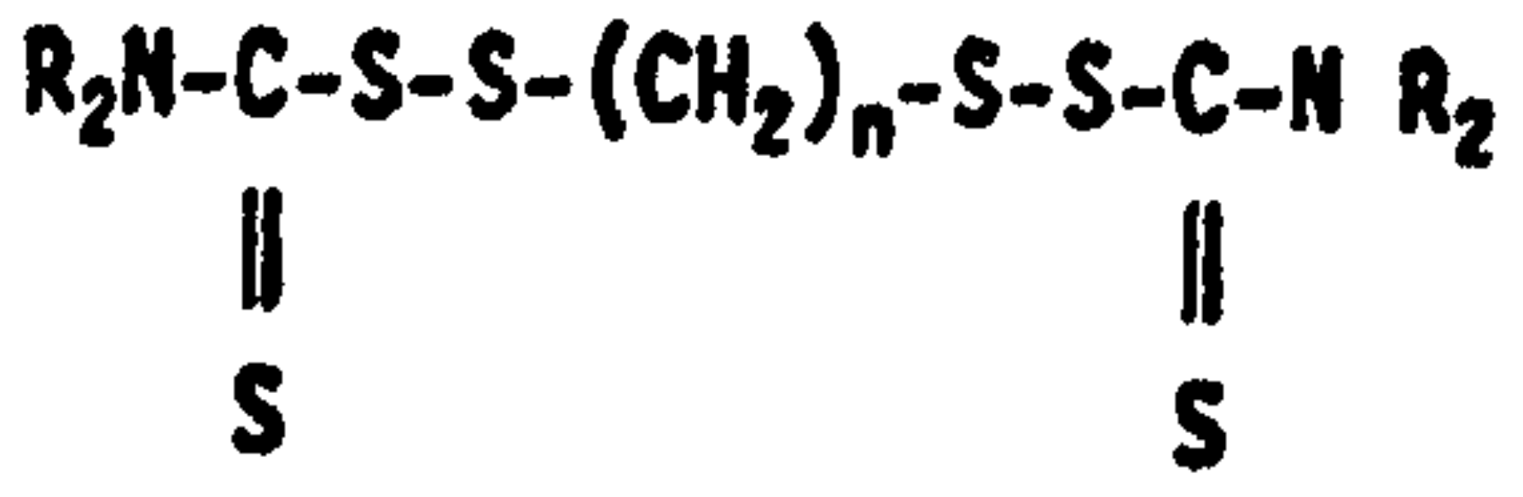
Anaerobic ageing is understood as meaning the behaviour of the vulcanisate with the exclusion of air, including, for example, in the heating mould, where prolonged reaction times cause so-called reversion in many diene rubbers. This is understood as meaning the decrease in important material properties, such as tensile strength, elongation at break, modulus and dynamic properties when the mixture is heated for longer than the optimum period of time. The phenomenon of reversion can be observed most simply with the aid of a so-called vulcameter curve in accordance with DIN 53 529.

Aerobic ageing, on the other hand, includes all processes of natural ageing in the presence of atmospheric oxygen, including at elevated temperatures, such as, for example, on vehicle tyres under operating conditions.

The deficiencies described in aerobic and anaerobic ageing are particularly pronounced in natural rubber and polyisoprene.

In order to compensate this disadvantage at least partly, in addition to using antioxidants, a number of alternative vulcanisation recipes have been used. These include so-called sulphur donors, such as tetramethylthiuram disulphide (TMTD), dimorpholine disulphide (DTDM) and similar compounds, or so-called EV systems which use the sulphur employed more efficiently by employing a larger amount of accelerator at a lower sulphur dosage. With these vulcanisation systems, however, the processing reliability is often impaired because of the shorter partial vulcanisation time. The vulcanisates produced with EV systems also have various disadvantages, including, in particular, their increased susceptibility to fatigue under continuous dynamic stress. When TMTD and generally low-molecular weight dithiocarbamates are employed, there is moreover the risk of the formation of a considerable amount of carcinogenic nitrosamines. Above all, however, the improvements which can be achieved in ageing stability are not yet convincing, but still mainly leave something to be desired.

Another way of improving the heat stability of diene rubber vulcanisates has been proposed in EP-OS 0 385 072 and 0 432 417: in this procedure, compounds which contain the customary radicals which accelerate sulphur vulcanisation and have the general structure



$$R_2N-\underset{\underset{S}{\|}}{C}-S-S-(CH_2)_n-S-S-\underset{\underset{S}{\|}}{C}-N\,R_2 \qquad (a)$$

- where R = ethyl and n = 2 (EP-OS 0 385 072), called BDTE below, and
- where R = benzyl and n = 2 (EP-OS 0 432 417) called BDBzTE below,
- and where n = 6, called BDBzTH below (EP-OS 0 432 417)

are employed as the sole crosslinking agents.

The examples demonstrate that, for example, vulcanisates having a very good ageing stability are to be obtained with 4.5 parts of BDTE or 7 parts of BDBzTE per 100 parts of rubber. BDBzTH with a longer network bridge is also used as a comparison example (EP-OS 0 432 417, Table 1a, Examples 1a and Da). However, the disadvantages of the system are also not to be left unmentioned:

a) BDTE is susceptible to the formation of hazardous nitrosamines.

b) The vulcanisation reaction proceeds considerably more slowly with the crosslinking agents BDBzTE and BDBzTH (t_{90} values of 29 minutes and 34.3 minutes), so that uneconomically long vulcanisation times of 40 minutes or more are required at 150°C.

c) Because of the high molecular weight of BDBzTE and BDBzTH, at least 7 parts must be employed per 100 parts of rubber in order to achieve useful vulcanisate properties, which represents an economic burden on the processes according to EP-OS 0 385 072 and 0 432 472.

Where such large amounts of chemicals are used, there is furthermore the risk that the secondary products formed in the course of the vulcanisation are no longer adequately soluble in the elastomer, but lead to undesirable efflorescence phenomena.

In both the patent documents mentioned, attention is drawn expressly to the adverse effect generally of sulphur additions in respect of the stability of the vulcanisate to reversion.

The abovementioned European patent applications thus provide no indication at all as to how diene rubber vulcanisates of outstanding ageing stability can be obtained with economically and industrially acceptable amounts of crosslinker substances over acceptable vulcanisation times.

The two DE-PSS 22 65.382 and 22 56 511 relate very generally to the compounds of the general formula

$$A\text{-}S\text{-}S\text{-}R\text{-}S\text{-}S\text{-}A' \qquad (b)$$

wherein the radicals A and A′ represent a large number of accelerator radicals, inter alia including N-substituted thiocarbamoyl radicals, and R represents almost any divalent organic radical. This results in an exceptionally wide selection of substances, of which some are employed in the examples. These also include an analogous substance according to the general formula (a) where R = methyl and n = 2, called BDMTE below. In DE-PS 22 65 382, this is also employed together with sulphur (column 31/32, Table VII), but the experiments show that even small amounts of sulphur (0.3 to 1 %) lead to undesirable reversion phenomena. It is expressly admitted that batches without addition of sulphur have a higher capacity for resistance to reversion (column 32, lines 1-11).

BDMTE and BDTE are employed as crosslinker substances in DE-PS 22 56 511. This specification refers to the adverse crosslinking density of the vulcanisates as a disadvantage (column 21, lines 12 to 27), which can be compensated by additions of 0.5 - 1.5 parts of sulphur, although the penalty again is an increased susceptibility of the rubber mixtures to reversion.

Generally, a criticism of the prior art last mentioned is that the absence of reversion phenomena in the rheometer test is used as the sole criterion of heat stability. However, as we have stated above, rheometer testing at best provides some information on anaerobic ageing - but even this is only incomplete, since the rheometer curve merely provides information on the torque of the vulcanisate. No data are given in DE-PSS 22 65 382 and 22 56 511 on the aerobic ageing resistance, which gives much more relevant indications of the resistance of the vulcanisate when used in practice. This information is preferably obtained by storage of vulcanisate samples in a circulating air cabinet under continuous exposure to a temperature of 100°C over a period of 3, 7 or 14 days (in accordance with DIN 53 508). After this time has elapsed, which represents exceptionally severe exposure for natural rubber, cis-polyisoprene, cis-polybutadiene and blends thereof, all the relevant elastomer properties are measured, such as tensile strength, elongation at break, modulus, hardness and rebound resilience, and if appropriate also the dynamic properties and the abrasion resistance. A comprehensive insight into the resistance of the elastomer to thermal ageing is thus obtained.

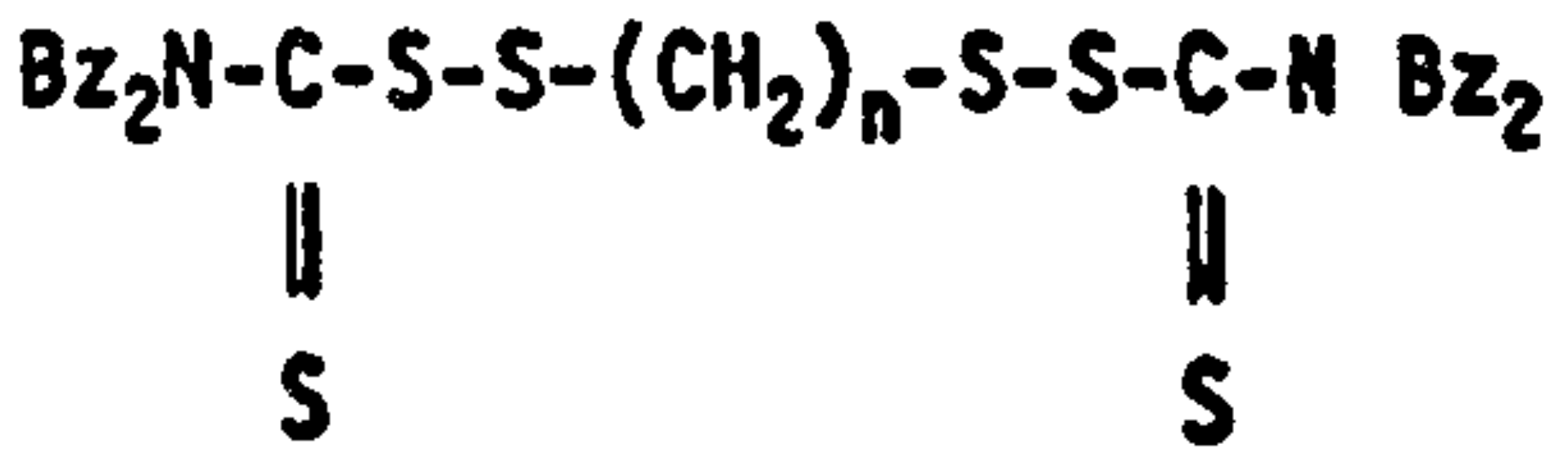
It therefore remains to state that the known prior art provides no usable process for obtaining, under appropriate conditions, heat- and ageing-stable vulcanisates of diene rubbers under practical use conditions.

The object of the present invention is thus to discover a heat-resistant, that is to say a both reversion-resistant and in particular ageing-stable crosslinking system for natural rubber and synthetic diene rubbers which avoids the disadvantages of the known systems. In detail, this means:

1. A vulcanisation rate as for conventional sulphur/accelerator systems.
2. A crosslinking yield, measured by the vulcanisate properties such as tensile strength, modulus and compression set, as with conventional sulphur/accelerator systems.
3. A resistance to reversion, that is to say anaerobic ageing resistance

4. An outstanding aerobic ageing resistance of the vulcanisates
5. A reduction in the amount of crosslinking agent used for technical reasons (risk of blooming) and also for economic reasons.

A solution to the problem, meeting all the preconditions, has now been achieved, surprisingly, by employing crosslinking agents having the formula



$$Bz_2N-\underset{\underset{S}{\|}}{C}-S-S-(CH_2)_n-S-S-\underset{\underset{S}{\|}}{C}-N\ Bz_2 \qquad (a)$$

where Bz = benzyl and n = 2 (BDBzTE) or
n = 6 (BDBzTH),

with the simultaneous use of very small, almost catalytic amounts of sulphur and in addition a small amount of a mercapto or sulphenamide accelerator, or mixtures thereof, as the vulcanisation system. The additional accelerator is used here for fine adjustment in controlling the vulcanisation kinetics.

Under the preconditions now found, the amount of crosslinking agents BDBzTE or BDBzTH employed in the vulcanisation of diene rubbers, such as natural rubber (NR), cis-polyisoprene (cis-IR), cis-polybutadiene (cis-BR), styrene-butadiene rubber (SBR) or blends thereof, can be reduced to 1 to 4.5 parts, preferably 2 to 4 parts, per 100 parts of rubber if simultaneously 0.05 to 0.3 part of sulphur, preferably 0.1 to 0.2 part, and 1 to 2.5 parts, preferably 1.3 to 1.8 parts, of a mercapto accelerator or 0.2 to 0.8 part, preferably 0.3 to 0.5 part, of a sulphenamide accelerator are employed, without the slightest curtailments having to be made in the mechanical properties after ageing compared with vulcanisates obtained from slow crosslinking with 6 to 7 parts of these crosslinking agents alone.

However, mixtures with 0.3 to 2.5 parts, particularly preferably 0.6 to 1.5 parts, of mercapto accelerator and 0.1 to 0.8 part, particularly preferably 0.2 to 0.6 part, of sulphenamide accelerator, in addition to the quantities of crosslinking agent and sulphur indicated above, are preferred.

The preferred accelerators used are zinc 2-mercaptobenzothiozole (ZMBT), dibenzothiazyl disulphide (MBTS) and N-tert-butyl-2-benzothiazyl-sulphenamide (TBBS), but it is quite possible within the scope of the invention to use other mercapto accelerators or sulphenamide accelerators.

The values found show that, compared with exclusive use of the crosslinking agents, significant improvements are even to be achieved. This result was in no way to be expected in view of the known adverse influence of sulphur on the reversion and ageing properties of elastomers.

Suitable diene rubbers are natural rubber, cis-polyisoprene, cis-polybutadiene and also conventional SBR, which can have been prepared by either solution or emulsion processes. Vinyl-polybutadiene and vinyl-SBR are suitable in the same way. It is also possible to use nitrile rubber and polyoctenamers (TOR). Equally good results are also obtained with blends of these polymers with one another. In addition, these rubbers can be used in the oil-free or oil-extended state.

The types of rubber listed are vulcanised in compounds of the usual composition, that is to say in mixtures which contain fillers, such as carbon blacks or silica, oils, rubber auxiliaries, zinc oxide, stearic acid, antioxidants and if appropriate ozone stabilisers in the customary amounts. However, it is not necessary to use the antioxidants mentioned (ASM) to obtain the action of the systems according to the invention. The system according to the invention also provides vulcanisates which have a considerable stability to ageing without ASM in the same way as ASM in a conventional system. The rubber mixtures are prepared in the customary manner in internal mixers (kneaders), and if appropriate also on roll mills.

The preparation of the crosslinker substances is described in detail in EP-OSS 0 385 072 and 0 432 417, so that it can be omitted here.

The vulcanisation of the finished mixtures can be carried out at the customary temperatures, that is to say at 140-200°C. The advantage of the system according to the invention is that vulcanisation can be carried out at higher temperatures without reversion phenomena with the known adverse effects on the vulcanisate properties becoming noticeable. Rubber articles are obtained which have an outstanding ageing resistance and are of great importance for various fields of use, such as, for example, for vehicle tyres, industrial elastomer articles, such as engine bearings and many other applications at elevated temperatures.

Accelerators based on triazine are in principle also possible, in addition to the abovementioned particularly preferred accelerators.

The advantages of the crosslinking systems according to the invention can be seen from the following examples. The properties shown in the tables are determined in accordance with the test specifications of the relevant DIN standards.

The tensile strength and elongation at break were determined in accordance with DIN 53 504.

The modulus at 100 and 300 % elongation was determined in accordance with DIN 53 504.

The tear strength was determined by the method of Pohle (compare S. Boström, Kautschuk-Handbuch [Rubber Handbook], Volume 5, page 123).

The permanent elongation (tension set) was determined in accordance with DIN 53 518.

The hardness (Shore A) was determined in accordance with DIN 53 505.

The rebound resilience (elasticity) was determined in accordance with DIN 53 512.

The abrasion was determined in accordance with DIN 53 516.

The compression set was determined in accordance with DIN 53 517.

The vulcametry was carried out in accordance with DIN 53 529.

The service life in the fatigue test was determined by the method of S. Boström, Kautschuk-Handbuch [Rubber Handbook], Volume 5, Berliner Union, Stuttgart, 1962, pages 149-150.

Examples 1-23 according to the invention shown in Tables 2 and 4 demonstrate the advance in ageing stability of diene rubber vulcanisates compared with the prior art and also compared with compositions of Comparison Examples I to XI of Tables 3 and 4, which are not according to the invention.

Examples 1 and 2 represent a preferred vulcanisation recipe with the base mixtures A (natural rubber) and B (cis-polyisoprene). The values after ageing for 14 days show that the residual elongation values (elongation at break of the vulcanisates after ageing for 14 days compared with the value of the non-aged vulcanisate) are still 73 and 78 % respectively. In contrast, Comparison

Example V (7 parts of BDBzTE in accordance with EP-0 432 417) has a residual elongation of only 62 %. Above all, however, the slow vulcanisation (t_{90} value 26.9 minutes) of the comparison example manifests itself in a completely unacceptable value for the compression set both at 70 and at 100°C.

Even increasing the vulcanisation temperature to 180°C led to no improvement: the t_{90} value was still 9.6 minutes, so that the vulcanisation time of 10 minutes which is customary at this temperature would also be inadequate. The economic disadvantages and the risk of blooming at such high dosages of crosslinker substance in Comparison Example V have already been dealt with.

In Comparison Example IV, a natural rubber mixture is vulcanised with a conventional thiuram system. After ageing in a circulating air cabinet at 100°C for 14 days, the disadvantages of thiuram vulcanisation over the system according to the invention are clearly revealed: not only has the residual elongation fallen to 57 % of the starting value; the tear strength according to Pohle (tear propagation resistance) has dropped sharply compared with the examples according to the invention. Damage to the vulcanisate can also be seen from the significantly reduced rebound resilience at 75°C.

An EV system shows similar disadvantages (Comparison Example II). Here also, the tear strength value, which has already dropped sharply after 7 days, and the rebound resilience at 75°C, which has fallen sharply after 14 days, very clearly demonstrate severe damage to the vulcanisate and therefore an inadequate ageing stability in comparison with the systems according to the invention.

A conventional sulphur accelerator system containing 0.6 part of sulphenamide accelerator and 2.5 parts of sulphur in a natural rubber mixture has been included as Comparison Example I in the table only for completeness: the values after ageing fall so extremely that practical use under exposure to heat cannot be considered at all.

However, the use of BDBzTE with a sulphenamide accelerator alone also does not achieve the aim, as Comparison Example III shows. Firstly, on the one hand, the vulcanisation is even slower than with 7 parts of BDBzTE alone, which manifests itself in an unacceptable compression set value. After ageing for 14 days, however, the decreasing values for the hardness and rebound resilience and the increasing compression set compared with the values after ageing for 7 days show that here also significant degradation is progressing in the vulcanisate.

Comparison Example VII shows the effect of too high a dosage of an accelerator, which is demonstrated by the example of a base mixture based on a cis-polyisoprene with the accelerator zinc 2-mercaptobenzothiazole (ZMBT). After ageing at 100°C for 14 days in a hot air cabinet, the severely reduced values of the tensile strength and tear strength according to Pohle' show that the vulcanisate of this comparison example is distinctly less resistant to ageing than Example 3 according to the invention, which has a clearly better retention of the physical values such as tensile strength, elongation at break and compression set.

In addition to the preferred embodiments of the invention corresponding to the Examples 1 and 2 described, modified recipes in the context of the preconditions according to the invention also lead to results which are clearly superior to the prior art.

The vulcanisation of cis-polyisoprene with 3 parts of BDBzTE and with 0.3 part of sulphur and 0.5 part of zinc 2-mercaptobenzothiazole (ZMBT) is described in Example 3.

The improved ageing stability compared with Comparison Example VII has already been referred to above.

BDBzTH is employed as the crosslinking agent in Examples 4 and 5. The examples show that the same outstanding ageing stability can be achieved with this crosslinking agent as with the crosslinking agent BDBzTE. When the hot air ageing is extended from 7 to 14 days, the tear propagation resistance (structure according to Pohle) does not drop noticeably, while the rebound resilience at 75°C, which is still increasing over the same period, shows no damage at all to the elastomer network. This result can be achieved in cis-polyisoprene neither with sulphur donors nor with EV systems.

Examples 6 to 8 show the use of BDBzTE with smaller amounts of sulphur and 0.4 to 0.6 part of the sulphenamide accelerator TBBS. The vulcanisation becomes somewhat slower as a result, but the compression set values both before and after ageing of the vulcanisates are clearly better than when the crosslinking agent alone is used, or with only the additional accelerator (Comparison Examples III and V). The values of the elongation at break after ageing at 100°C for 14 days in relation to the starting values before ageing are exceptionally high particularly in Examples 6 and 7, at 80 and 74 % respectively. These examples show that an increase in the dosage of BDBzTE does not necessarily give better values in all criteria.

Examples 9 and 10 show the vulcanisation of styrene-butadiene rubber (SBR) by 3 to 4 parts of the crosslinking agent BDBzTE and addition of 0.1 to 0.2 part of sulphur and 0.4 part of the additional accelerator TBBS. Outstanding abrasion and compression set values are achieved in both vulcanisates after ageing for 14 days, and in the recipe according to Example 10 a lower increase in hardness and higher residual elongation are also achieved.

These two examples show that in SBR, which is known to tend to harden under aerobic ageing, a lower dosage of sulphur and an amount of the crosslinking agent BDBzTE or BDBzTH tending towards the upper limit produce more favourable results if an increase in modulus which is as low as possible is sought.

Comparison Examples VIII to X illustrate the effects of a sulphur dosage in an SBR mixture which has been increased to 0.3 to 0.6 part, in comparison with Examples 9 and 10 (0.2 and 0.1 part of sulphur respectively), and in particular both with the additional accelerator TBBS (X : 0.2 part) and without this (VIII and IX). After 14 days at 100°C, the residual elongations of the mixtures without an additional accelerator fall to only 18 to 27 % of the starting value. In Comparison Example VIII also, the residual values for the tensile strength and elongation at break after ageing in a circulating air cabinet at 100°C for 14 days are at a clearly lower level than in the case of Examples 9 and 10 according to the invention, so that the effectiveness of the process according to the invention is clearly demonstrated.

The effect of too high a sulphur dosage on a polyisoprene mixture is demonstrated in Comparison Example VI (the amount of additional accelerator TBBS was reduced from 0.4 to 0.2 part in order to achieve comparable moduli in the vulcanisates). If this example is compared with Example 2 according to the invention with 0.2 part of sulphur, it is striking that the elongation has already fallen to < 300 % (64 % of the starting value, compared with 77 % in Example 2) after ageing at 100°C for 7 days. The tear strength is also lower from the beginning at a higher sulphur dosage.

While the level of properties in Example 2 has scarcely fallen further after 14 days at 100°C compared with 7 days, a distinct further drop in the tensile strength, elongation and elasticity are found in Comparison Example VI, which indicates damage to the network. The system according to the invention thus acts on cis-polyisoprene in the same way as on SBR.

Example 11 shows the vulcanisation of a blend of natural rubber, cis-polybutadiene and SBR, such as is found in a tread mixture for winter tyres, with the crosslinking system according to the invention. Here also, excellent retention of the compression set and the rebound resilience are to be observed.

In a further preferred embodiment, dibenzothiazyl disulphide (MBTS) is very advantageously used, either in combination with TBBS or alone. In this case, it is possible to shorten the vulcanisation times even further. Thus, a polyisoprene mixture according to Examples 14 and 15 shows a t_{90} value of only 14-15 minutes. At the same time, the dosage of BDBzTH can be lowered from 3.3 to 2.5 parts, without the modulus of the vulcanisate falling. Looking at the ageing properties, it becomes clear that, in spite of the reduced amount of BDBzTH, outstanding values of structural strength, hardness and elasticity are obtained, similar to those in Examples 2 and 4.

However, the amount of this additional accelerator alone must not be kept too low. With only 0.8 part of MBTS (Comparison Example XI), an inadequate vulcanisate and unfavourable ageing values after 14 days at 100°C are obtained, and this manifests itself particularly in a low tear strength and rebound resilience and in more extensive heating in the service life fatigue test.

Examples 17-19 demonstrate the advantages of the process according to the invention in the use of MBTS as an additional accelerator of SBR. After ageing for 14 days at 100°C, the tensile strength of the vulcanisate is still 20 MPa and the elongation at break of the same samples is still 380 - 500%, whereas only 6-11.8 MPa tensile strength and 69 - 196% elongation at break are obtained in comparison Examples VIII-X.

The process according to the invention is also particularly suitable for vulcanising oil-extended rubbers. This is demonstrated by Examples 20 to 23. As can be seen from Table 4, good vulcanisation states are obtained with a combination of TBBS and MBTS as additional accelerators (Example 20) or also with MBTS alone (Examples 21 to 22). The table also shows the excellent residual values for tensile strength, elongation at break, tear strength according to Pohle and compression set, and for the dynamic values coupled at the same time with only moderately increasing hardness, after 14 days ageing at 100°C.

By contrast, only 6 - 11.8 MPa tensile strength and 69 - 196% elongation at break are obtained in Comparison Examples VIII-X.

Examples 1 to 23 demonstrate the advantages of the process according to the invention in comparison with Comparison Examples I to XI which are not according to the invention:

The use of only 2 to 4 parts of the crosslinker substances BDBzTE or BDBzTH according to the invention per 100 parts of rubber while simultaneously using 0.05 to 0.3, but preferably 0.1 to 0.2 part of sulphur and 0.3 to 2.5, but in particular 0.5 to 1.8 part of a mercapto accelerator, such as zinc 2-mercaptobenzothiazole (ZMBT), 2-mercaptobenzothiazole (MBT) or dibenzothiazyl disulphide (MBTS), or 0.1 to 0.8, preferably 0.3 to 0.5, part of a sulphenamide accelerator, such as N-tert-butyl-2-benzothiazylsulphenamide (TBBS), but amongst these preferably TBBS or ZMBT; furthermore, especially mixtures of 0.7 to 1.8 parts of a mercapto accelerator and 0.2 to

0.6 part of a sulphenamide accelerator, MBTS and TBBS being preferably used here.

Elastomers having a previously unachieved outstanding ageing resistance and reversion resistance are obtained after relatively short vulcanisation times using economical amounts and avoiding blooming phenomena in the vulcanisate.

Table 1:

B A S E M I X T U R E	A	B	C	D	E	F	G	H
NR (RSS # Defo 1000)	100	-	-	50	100	-	-	-
cis-IR[1]	-	100	-	-	-	100	-	-
E-SBR 1502[2]	-	-	100	20	-	-	100	-
E-SBR 1712[3]	-	-	-	-	-	-	-	137.5
BR[4]	-	-	-	30	-	-	-	-
ZnO RS	3	3	3	3	3	3	3	3
Stearic acid	2	2	2	2	2	2	2	2
IPPD[5]	1	1	1	1	1	1	1	1
6PPD[6]	1	1	1	1	1	1	1	1
Koresin	1	1	1	-	-	-	-	-
Carbon black N-33945	45	45	45	50	45	45	50	75
HAR oil	-	-	-	10	-	-	10	2

[1] NATSYN^{R} 2200, Goodyear

[2] Styrene-butadiene copolymer, styrene content 23.5 %, ML (1 + 4) 100°C = 50, polymerized in aqueous emulsion, Hüls AG

[3] Styrene-butadiene copolymer, styrene content 23.5 %, ML (1 + 4) 100°C = 49, extended with 37.5 parts of highly aromatic oil, Hüls AG

[4] Cis-polybutadiene, cis-1,4 content at least 95 %, ML (1 + 4) 100°C = 46 ± 4, Hüls AG

[5] N-Isopropyl-N'-phenyl-p-phenylenediamine

[6] N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine

Table 2:

Base mixture		A	B	B	B	B	B	B	B	C	C	D
Sulphur		0.2	0.2	0.3	0.2	0.1	0.1	0.1	0.05	0.2	0.1	0.2
TBBS		0.4	0.4	-	0.4	0.4	0.4	0.6	0.4	0.4	0.4	0.4
ZMBT		-	-	0.5	-	-	-	-	-	-	-	-
BDBzTE		3.0	3.0	3.0	-	-	3.0	3.0	4.0	3.0	4.0	-
BDBzTH		-	-	-	3.3	4.4	-	-	-	-	-	3.3
Example		1	2	3	4	5	6	7	8	9	10	11
Vulcameter 150°C												
t_{10}	min.	8.7	8.6	6.9	9.5	12.0	9.9	9.4	10.2	11.7	11.7	9.2
t_{90}	min.	21.9	24.2	19.0	22.3	25.9	27.4	25.9	27.9	26.8	25.3	20.4
Vulcanisation 30 minutes at 150°C												
Tensile strength	MPa	23.2	21.0	18.7	22.2	20.1	19.2	20.8	19.0	20.4	17.3	18.2
Elongation at break	%	516	545	466	582	566	534	591	567	559	492	482
Modulus 100 %	MPa	2.3	1.7	2.0	1.6	1.5	1.5	1.4	1.3	1.9	1.8	2.8
Modulus 300 %	MPa	12.5	9.2	10.5	9.0	8.5	8.6	7.8	7.6	9.5	9.4	10.0
Tear strength according to Pohle	N/mm	87	71	76	81	85	73	75	82	31	40	56

Continuation of Table 2:

Example		1	2	3	4	5	6	7	8	9	10	11
Hardness												
22°C	Sh.A	65	63	66	60	62	58	59	60	64	65	69
75°C	Sh.A	55	53	57	51	51	48	49	50	56	55	59
Elasticity												
22°C	%	47	47	48	48	45	47	48	45	46	46	40
75°C	%	57	58	60	60	52	57	58	54	55	54	56
Compression set												
24 h/ 70°C		25	16	20	21	21	18	19	21	28	30	20
24 h/100°C		41	34	32	34	42	40	42	46	49	54	-
DIN abrasion	mm^3	142	162	143	120	-	212	190	201	99	98	80

Continuation of Table 2:

Base mixture		A	B	B	B	B	B	B	B	C	C	D
Sulphur		0.2	0.2	0.3	0.2	0.1	0.1	0.1	0.05	0.2	0.1	0.2
TBBS		0.4	0.4	-	0.4	0.4	0.4	0.6	0.4	0.4	0.4	0.4
ZMBT		-	-	0.5	-	-	-	-	-	-	-	-
BDBzTE		3.0	3.0	3.0	-	-	3.0	3.0	4.0	3.0	4.0	-
BDBzTH		-	-	-	3.3	4.4	-	-	-	-	-	3.3
		after ageing for 7 days/100°C										
Example		1	2	3	4	5	6	7	8	9	10	11
Vulcanisation for 30 minutes at 150°C												
Tensile strength	MPa	17.8	18.4	17.3	21.5	19.4	18.8	19.5	16.5	19.8	18.8	13.5
Elongation at break	%	375	425	363	474	429	470	474	408	399	353	322
Modulus 100 %	MPa	3.5	2.7	3.1	2.7	2.7	2.0	2.3	2.3	3.2	3.7	3.1
Modulus 300 %	MPa	15.2	13.0	15	13.1	13.3	10.9	11.6	11.9	15.4	16.7	12.9
Tear strength according to Pohle	N/mm	51	56	50	66	71	66	63	65	28	34	58

Continuation of Table 2:

Example		after ageing for 7 days/100°C										
		1	2	3	4	5	6	7	8	9	10	11
Hardness												
22°C	Sh.A	70	70	72	69	70	66	68	68	72	69	74
75°C	Sh.A	62	59	64	59	61	57	58	59	63	62	66
Elasticity												
22°C	%	52	52	54	52	52	51	49	51	49	52	41
75°C	%	59	58	62	58	56	57	56	57	60	61	56
Compression set												
24 h/ 70°C		22	20	20	18	18	21	17	19	20	18	22
24 h/100°C		23	19	22	21	22	21	23	24	21	24	-
DIN abrasion	mm³	-	-	171	191	-	160	262	168	126	121	112

Continuation of Table 2:

Base mixture		A	B	B	B	B	B	B	B	C	C	D
Sulphur		0.2	0.2	0.3	0.2	0.1	0.1	0.1	0.05	0.2	0.1	0.2
TBBS		0.4	0.4	-	0.4	0.4	0.4	0.6	0.4	0.4	0.4	0.4
ZMBT		-	-	0.5	-	-	-	-	-	-	-	-
BDBzTE		3.0	3.0	3.0	-	-	3.0	3.0	4.0	3.0	4.0	-
BDBzTH		-	-	-	3.3	4.4	-	-	-	-	-	3.3
		after ageing for 14 days/100°C										
Example		1	2	3	4	5	6	7	8	9	10	11
Vulcanisation for 30 minutes at 150°C												
Tensile strength	MPa	14.5	16.6	15.2	15.9	14.5	16.9	18.5	14.2	15.8	19.2	12.6
Elongation at break	%	343	390	339	379	352	425	435	343	256	355	280
Modulus 100 %	MPa	3.1	2.8	3.3	2.6	2.8	2.3	2.6	2.8	5.2	3.9	4.0
Modulus 300 %	MPa	13.8	13.3	14.7	13.5	13.5	11.9	12.7	13.5	-	18	-
Tear strength according to Pohle	N/mm	48	53	49	55	60	59	58	55	23	27	54

Continuation of Table 2:

		after ageing for 14 days/100°C										
Example		1	2	3	4	5	6	7	8	9	10	11
Hardness												
22°C	Sh.A	69	69	72	69	72	66	66	68	74	73	76
75°C	Sh.A	58	61	65	59	63	58	58	60	64	66	68
Elasticity												
22°C	%	47	52	53	52	52	50	52	53	50	51	41
75°C	%	57	58	61	60	57	57	58	58	59	59	57
Compression set												
24 h/ 70°C		29	21	19	26	22	20	20	21	19	18	22
24 h/100°C		35	25	25	24	25	24	26	23	24	21	-
DIN abrasion	mm^3	-	-	200	182	-	195	166	168	116	113	128

Table 3:

Base mixture		A	A	A	A	A	B	B	C	C	C
Sulphur		2.5	0.4	-	0.6	-	0.5	0.1	0.3	0.5	0.6
TBBS		0.6	1.2	0.8	0.8	-	0.2	-	-	-	0.2
ZMBT		-	-	-	-	-	-	1.0	-	-	-
TMTD 80 %		-	-	-	0.4	-	-	-	-	-	-
BDBzTE		-	-	3.0	-	7.0	3.0	3.0	3.0	3.0	3.0
Comp. Example		I	II	III	IV	V	VI	VII	VIII	IX	X
Vulcameter 150°C											
t_{10}	min.	6.8	8.4	11.6	4.5	10.0	7.7	6.5	14.3	13.0	10.6
t_{90}	min.	14.6	14.4	30.3	7.6	26.9	17.1	21.6	31.6	30.2	24.5
Vulcanisation 30 minutes at 150°C											
Tensile strength	MPa	20.4	19.5	17.7	23.6	18.2	16.7	19.4	17.2	14.8	14.3
Elongation at break	%	512	528	561	568	461	417	583	492	377	346
Modulus 100 %	MPa	2.0	1.5	1.3	1.8	1.9	2.2	1.4	2	2.5	2.5
Modulus 300 %	MPa	9.8	9.2	7.8	10.8	10.9	11.5	7.2	9.7	12.2	13.3
Tear strength according to Pohle	N/mm	67	66	57	74	44	69	62	33	29	32

Continuation of Table 3:

Comp. Example		I	II	III	IV	V	VI	VII	VIII	IX	X
Hardness											
22°C	Sh.A	58	55	57	59	67	67	60	65	68	67
75°C	Sh.A	48	44	40	48	53	59	50	54	59	59
Elasticity											
22°C	%	50	50	45	52	39	48	47	48	46	48
75°C	%	59	58	50	59	50	60	58	55	57	59
Compression set											
24 h/ 70°C26		36	53	28	46	16	21	33	25	20	
24 h/100°C -		-	-	-	69	28	40	56	44	36	
DIN abrasion	mm^3	105	-	-	-	-	-	187	-	-	108

Continuation of Table 3:

Base mixture		A	A	A	A	A	B	B	C	C	C
Sulphur		2.5	0.4	-	0.6	-	0.5	0.1	0.3	0.5	0.6
TBBS		0.6	1.2	0.8	0.8	-	0.2	-	-	-	0.2
ZMBT		-	-	-	-	-	-	1.0	-	-	-
TMTD 80 %		-	-	-	0.4	-	-	-	-	-	
BDBzTE		-	-	3.0	-	7.0	3.0	3.0	3.0	3.0	3.0
		after ageing for 7 days/100°C									
Comp. Example		I	II	III	IV	V	VI	VII	VIII	IX	X
Vulcanisation 30 minutes at 150°C											
Tensile strength	MPa	13.5	11.1	19.1	11.7	11.8	11.3	19.0	18.0	13.9	12.6
Elongation at break	%	272	391	466	353	279	269	469	345	251	216
Modulus 100 %	MPa	3.2	1.9	2.7	2.4	3.3	3.2	2.3	3.6	4.3	4.8
Modulus 300 %	MPa	-	8.2	12.4	10.7	-	-	11.2	16.7	-	-
Tear strength according to Pohle	N/mm	42	13	62	35	52	42	62	31	24	27

Continuation of Table 3:

		after ageing for 7 days/100°C									
Comp. Example		I	II	III	IV	V	VI	VII	VIII	IX	X
Hardness											
22°C	Sh.A	67	61	67	63	70	70	68	69	74	73
75°C	Sh.A	57	49	57	50	62	63	58	64	66	66
Elasticity											
22°C	%	50	46	50	48	49	56	53	49	50	51
75°C	%	56	60	55	53	54	62	60	61	63	62
Compression set											
24 h/ 70°C24		28	24	26	22	22	25	17	15	20	
24 h/100°C -		-	-	-	26	20	30	23	17	16	
DIN abrasion	mm^3	214	-	-	-	177	-	199	108	122	122

Continution of Table 3:

Base mixture	A	A	A	A	A	B	B	C	C	C
Sulphur	2.5	0.4	-	0.6	-	0.5	0.1	0.3	0.5	0.6
TBBS	0.6	1.2	0.8	0.8	-	0.2	-	-	-	0.2
ZMBT	-	-	-	-	-	-	1.0	-	-	-
TMTD 80 %	-	-	-	0.4	-	-	-	-	-	-
BDBzTE	-	-	3.0	-	7.0	3.0	3.0	3.0	3.0	3.0
				after ageing for 14 days at 100°C						
Comp. Example	I	II	III	IV	V	VI	VII	VIII	IX	X
Vulcanisation 30 minutes at 150°C										
Tensile strength MPa	3.4	6.6	16.2	9.6	11.3	9.8	5.9	9.2	6.0	11.8
Elongation at break %	58	311	429	323	284	234	265	132	69	196
Modulus 100 % MPa	-	1.7	2.5	2.1	3.1	3.1	1.9	7.3	-	5.2
Modulus 300 % MPa	-	6.5	11.8	9.5	-	-	-	-	-	-
Tear strength according to Pohle N/mm	11	12	53	15	51	39	33	21	16	25

Continuation of Table 3:

Comp. Example		after ageing for 14 days at 100°C									
		I	II	III	IV	V	VI	VII	VIII	IX	X
Hardness											
22°C	Sh.A	73	60	64	62	72	71	67	73	76	83
75°C	Sh.A	63	47	54	50	64	63	58	65	68	74
Elasticity											
22°C	%	43	42	43	38	49	53	51	51	50	52
75°C	%	53	45	49	45	58	58	58	60	60	61
Compression set											
24 h/ 70°C		28	40	35	37	23	24	24	15	18	19
24 h/100°C		-	-	-	-	33	29	37	21	25	20
DIN											
abrasion	mm^3	265	-	-	-	-	-	190	113	118	172

Table 4 / Base Mixture E:

Recipe		12	13	XI
Sulphur		0.2	0.2	0.2
TBBS		0.4	0.0	0.0
MBTS		1.0	1.5	0.0
BDBzTH		2.5	2.5	3.5
Vulcameter 150 °C, t_{10}	min.	4.8	4.1	11
t_{90}	min.	14.2	13.2	25.6
Vulcameter 180 °C, t_{10}	min.	1.6	1.4	2.5
t_{90}	min.	3.4	3.1	4.4
Vulcanisation at 180 °C	**min**	**10**	**10**	**10**
Tensile strength	Mpa	23.1	25.1	22
Elongation at break	%	512	519	529
Modulus at 100 % elongation	Mpa	2.1	2.2	1.9
Modulus at 300 % elongation	Mpa	12.7	13.4	11.1
Tear strength according to Pohle	N/mm	77	81	70
Tension set	%	10	10	12
Hardness 22 °C	Shore A	64	63	62
Hardness 75 °C	Shore A	54	53	52
Elasticity 22 °C	%	48	51	45
Elasticity 75 °C	%	59	62	54
Compression set 24 h/ 70 °C	%	17	17	25
Compression set 24/h 100 °C	%	33	31	35
DIN abrasion	mm^3	160	147	176
Vulcanisation at 180 °C	**min**	**20**	**20**	**20**
Fatigue test 150 N	°C	106	101	159
200 N	°C	146	139	12′
250 N	°C	14.8′	14.8′	
Goodrich Method 5	°C	32	34	deformation too high
Deformation	%	-0.8	-1.5	

': Time interval (minutes) for the destruction of the ball fartique under the condition mentioned in the table.

Continuation of Table 4 / Base Mixture E:

Recipe		12	13	XI
Ageing for 7 days at 100°C				
Tensile strength	Mpa	20.1	20.5	16.9
Elongation at break	%	421	412	405
Modulus at 100 % elongation	MPa	2.7	3	2.6
Modulus at 300 % elongation	MPa	14.5	15.5	12.9
Tear strength according to Pohle	N/mm	70	68	25
Tension set	%	6	8	8
Hardness 22 °C	Shore A	67	68	69
Hardness 75 °C	Shore A	58	58	57
Elasticity 22 °C	%	49	51	47
Elasticity 75 °C	%	59	61	52
Compression set 24 h/ 70 °C	%	14	12	21
Compression set 24/h 100 °C	%	25	23	24
DIN abrasion	mm^3	161	160	171
Fatigue test 150 N	°C	88	79	104
200 N	°C	118	108	144
250 N	°C	139	126	186
300 N	°C	159	150	6′
350 N	°C	13′	179	
400 N	°C		8′	

Continuation of Table 4 / Base Mixture E:

Recipe		12	13	XI
Ageing for 14 days at 100°C				
Tensile strength	Mpa	20.2	18.8	10.2
Elongation at break	%	429	406	350
Modulus at 100 % elongation	MPa	2.9	2.9	2
Modulus at 300 % elongation	MPa	14.5	14.9	9.3
Tear strength according to Pohle	N/mm	61	60	13
Tension set	%	10	11	10
Hardness 22 °C	Shore A	66	66	65
Hardness 75 °C	Shore A	57	56	49
Elasticity 22 °C	%	49	52	42
Elasticity 75 °C	%	56	59	46
Compression set 24 h/ 70 °C	%	22	20	33
Compression set 24/h 100 °C	%	35	34	40
DIN abrasion	mm^3	175	169	234
Fatigue test 150 N	°C	82	81	104
200 N	°C	114	111	140
250 N	°C	137	132	175
300 N	°C	159	154	8′
350 N	°C	187	177	
400 N	°C	5′	5′	

Table 4 / Base Mixture F:

Recipe		14	15	16	XI
Sulphur		0.2	0.2	0.1	0.2
TBBS		0.4	0.0	0.0	0.0
MTBS		1.0	1.5	1.5	0.8
BDBzTH		2.5	2.5	3.5	3.5
Vulcameter 150 °C, t_{10}	min.	4.4	4.1	5	10.5
t_{90}	min.	15.3	14.5	19.5	22.6
Vulcameter 180 °C, t_{10}	min.	1.4	1.3	1.7	2.5
t_{90}	min.	3.8	3.7	4.4	4.5
Vulcanisation at 180 °C	**min**	**10**	**10**	**10**	**10**
Tensile strength	Mpa	22.6	21.2	21.4	20.4
Elongation at break	%	556	522	559	584
Modulus at 100 % elongation		1.8	1.8	1.7	1.4
Modulus at 300 % elongation		10.2	10.1	9.1	7.9
Tear strength according to Pohle	N/mm	63	74	65	62
Tension set	%	10	10	10	10
Hardness 22 °C	Shore A	62	61	62	56
Hardness 75 °C	Shore A	52	52	51	48
Elasticity 22 °C	%	48	49	47	46
Elasticity 75 °C	%	60	60	57	57
Compression set 24 h/70 °C	%	12	12	15	17
Compression set 24 h/100°C	%	25	24	31	27
DIN abrasion	mm^3	158	162	169	164
Vulcanisation at 180 °C	**min**	**20**	**20**	**20**	**20**
Fatigue test 150 N	°C	101	100	109	120
200 N	°C	127	129	133	158
250 N	°C	151	159	176	11'
Goodrich Method 5	°C	29	29	30	38

Continuation of Table 4/Base Mixture F:

Recipe		14	15	16	XI
Ageing for 7 days at 100 °C					
Tensile strength	MPa	21.3	20.5	19.3	20.2
Elongation at break	%	487	463	441	494
Modulus at 100% elongation	MPa	2.5	2.5	2.5	2.2
Modulus at 300% elongation	MPa	12.5	12.8	12.8	11.1
Tear strength according to Pohle	N/mm	64	69	63	65
Tension set	%	10	8	7	10
Hardness 22 °C	Shore A	68	68	67	66
Hardness 75 °C	Shore A	58	60	59	57
Elasticity 22 °C	%	50	52	52	58
Elasticity 75 °C	%	59	61	60	54
Compression set 24 h/ 70 °C	%	15	14	11	18
Compression set 24 h/100 °C	%	23	23	22	24
DIN abrasion	mm^3	168	173	173	183
Fatigue test 150 N	°C	89	89	101	105
200 N	°C	117	117	127	138
250 N	°C	136	137	147	157
300 N	°C	157	156	169	14.8′
350 N	°C	189	168	9′	
400 N	°C	5′	5′		
Goodrich Method 5	°C	37	34	35	43
Deformation	%	0.6	±0.0	-0.5	-1.2

Continuation of Table 4/Base Mixture F:

Recipe			14	15	16	XI
Ageing for 14 days at 100 °C						
Tensile strength		MPa	18.3	21.2	20.1	18.6
Elongation at break		%	439	478	461	474
Modulus at 100% elongation		MPa	2.6	2.5	2.6	2.3
Modulus at 300% elongation		MPa	12.3	12.5	12.7	11.1
Tear strength according to Pohle		N/mm	51	48	54	27
Tension set		%	9	10	9	10
Hardness	22 °C	Shore A	66	70	68	64
Hardness	75 °C	Shore A	58	59	60	55
Elasticity	22 °C	%	50	50	40	48
Elasticity	75 °C	%	59	57	59	52
Compression set 24 h/ 70 °C		%	21	23	19	24
Compression set 24 h/100 °C		%	32	31	33	33
DIN abrasion		mm³	177	178	177	199
Fatigue test 150 N		°C	89	90	921	104
200 N		°C	117	120	125	135
250 N		°C	138	139	143	160
300 N		°C	158	157	157	14.8′
350 N		°C	188	178	14.8′	
400 N		°C	7′	7′		
Goodrich Method 5		°C	41	39	41	54
Deformation		%	-2.1	-1.6	-2.1	-0.9

Table 4 / Base Mixture G:

Recipe		17	18	19
Sulphur		0.2	0.1	0.2
TBBS		0.0	0.4	0.4
MBTS		1.5	1.5	1.5
BDBzTH		3.0	3.5	2.0
Vulcameter 150 °C, t_{10}	min.	9.8	10.9	9.5
t_{90}	min.	23.8	25.8	22.1
Vulcameter 180 °C, t_{10}	min.	2.5	2.7	2.4
t_{90}	min.	5	5.8	5.1
Vulcanisation at 180 °C	**min**	10	10	10
Tensile strength	MPa	20.3	22.9	22.5
Elongation at break	%	535	590	632
Modulus at 100 % elongation	MPa	2	1.9	1.7
Modulus at 300 % elongation	MPa	10.4	9.9	8.8
Tear strength according to Pohle	N/mm	43	46	48
Tension set	%	10	11	13
Hardness 22 °C	Shore A	63	62	62
Hardness 75 °C	Shore A	55	53	52
Elasticity 22 °C	%	43	43	43
Elasticity 75 °C	%	53	53	52
Compression set 24 h/70 °C	%	17	20	19
Compression set 24 h/100°C	%	34	43	36
DIN abrasion	mm^3	112	115	115
Vulcanisation at 180 °C	**min**	20	20	20
Fatigue test 150 N	°C	98	103	112
200 N	°C	126	155	187
250 N	°C	151	155	187
300 N	°C	175	178	187
350 N	°C	7′	10′	6′
Goodrich Method 5	°C	44	47	55
Deformation	%	-0.8	-1.9	-1.8

Continuation of Table 4/Base Mixture G:

Recipe		17	18	19
Ageing for 7 days at 100 °C				
Tensile strength	MPa	21.2	20.6	22.2
Elongation at break	%	447	465	556
Modulus at 100% elongation	MPa	2.8	2.9	2.4
Modulus at 300% elongation	MPa	14.2	14.4	11.8
Tear strength according to Pohle	N/mm	36	36	43
Tension set	%	7	7	11
Hardness 22 °C	Shore A	67	66	64
Hardness 75 °C	Shore A	59	59	56
Elasticity 22 °C	%	47	47	46
Elasticity 75 °C	%	57	57	54
Compression set 24 h/ 70 °C	%	12	12	14
Compression set 24 h/100 °C	%	21	24	22
DIN abrasion	mm³	122	120	117
Fatigue test 150 N	°C	89	94	100
200 N	°C	119	119	132
250 N	°C	138	146	159
300 N	°C	158	169	183
350 N	°C	181	14′	8′
400 N	°C	6′		
Goodrich Method 5	°C	44	43	53
Deformation	%	0.8	1	-0.8

Continuation of Table 4/Base Mixture G:

Recipe		17	18	19
Ageing for 14 days at 100 °C				
Tensile strength	MPa	19.5	20.4	21.4
Elongation at break	%	382	401	496
Modulus at 100% elongation	MPa	3.5	3.4	2.9
Modulus at 300% elongation	MPa	16.3	15.9	13.2
Tear strength according to Pohle	N/mm	32	30	35
Tension set	%	6	6	10
Hardness 22 °C	Shore A	72	72	71
Hardness 75 °C	Shore A	63	63	45
Elasticity 22 °C	%	46	46	45
Elasticity 75 °C	%	56	56	52
Compression set 24 h/ 70 °C	%	14	13	18
Compression set 24 h/100 °C	%	18	21	24
DIN abrasion	mm³	125	131	123
Fatigue test 150 N	°C	92	96	102
200 N	°C	120	123	135
250 N	°C	140	145	156
300 N	°C	160	164	180
350 N	°C	184	188	11.5′
400 N	°C	6.5′	3′	
Goodrich Method 5	°C	42	44	55
Deformation	%	-1.0	-0.7	-4.1

Table 4 / Base Mixture H:

Recipe		20	21	22	23
Sulphur		0.2	0.2	0.3	0.2
TBBS		0.4	0.0	0.0	0.4
MBTS		0.8	1.5	1.5	1.0
BDBzTH		4.0	4.0	3.5	3.5
Vulcameter 150 °C, t_{10}	min.	12	10.9	10.3	11.8
t_{90}	min.	26.2	25.5	22.3	24.3
Vulcameter 180 °C, t_{10}	min.	2.8	2.5	2.3	2.6
t_{90}	min.	5	5	4.6	4.8
Vulcanisation at 180 °C	min	10	10	10	10
Tensile strength	MPa	19.5	19	18.6	19
Elongation at break	%	510	518	489	531
Modulus at 100 % elongation	MPa	2.1	2	2.2	1.9
Modulus at 300 % elongation	MPa	11.3	10.7	11.6	10.6
Tear strength according to Pohle	N/mm	36	37	37	41
Tension set	%	11	11	11	11
Hardness 22 °C	Shore A	63	63	65	61
Hardness 75 °C	Shore A	53	54	56	52
Elasticity 22 °C	%	33	33	32	33
Elasticity 75 °C	%	51	49	48	49
Compression set 24 h/70 °C	%	16	17	14	18
Compression set 24 h/100°C	%	33	34	30	33
DIN abrasion	mm^3	108	111	124	116
Vulcanisation at 180 °C	min	20	20	20	20
Fatigue test 150 N	°C	105	110	109	114
200 N	°C	140	144	141	154
250 N	°C	166	181	176	189
300 N	°C	14.8′	7′	10′	5′
Goodrich Method 5	°C	51	49	47	51
Deformation	%	-1.2	-0.4	0.4	-1.3

Continuation of Table 4/Base Mixture H:

Recipe		20	21	22	23
Ageing for 7 days at 100 °C					
Tensile strength	MPa	18.2	17.7	17.3	18
Elongation at break	%	426	424	394	462
Modulus at 100% elongation	MPa	3	3.1	3.3	2.9
Modulus at 300% elongation	MPa	13.8	13.9	14.4	13
Tear strength according to Pohle	N/mm	36	34	35	39
Tension set	%	11	11	10	15
Hardness 22 °C	Shore A	66	66	66	66
Hardness 75 °C	Shore A	57	57	57	57
Elasticity 22 °C	%	36	36	36	36
Elasticity 75 °C	%	49	49	50	46
Compression set 24 h/ 70 °C	%	15	13	13	15
Compression set 24 h/100 °C	%	23	22	20	23
DIN abrasion	mm^3	138	126	134	135
Fatigue test 150 N	°C	103	102	99	106
200 N	°C	138	133	132	135
250 N	°C	159	155	156	161
300 N	°C	14′	178	178	192
350 N	°C		12′	14.8′	5′
Goodrich Method 5	°C	55	50	50	55
Deformation	%	-0.6	-0.7	-0.2	-1.2

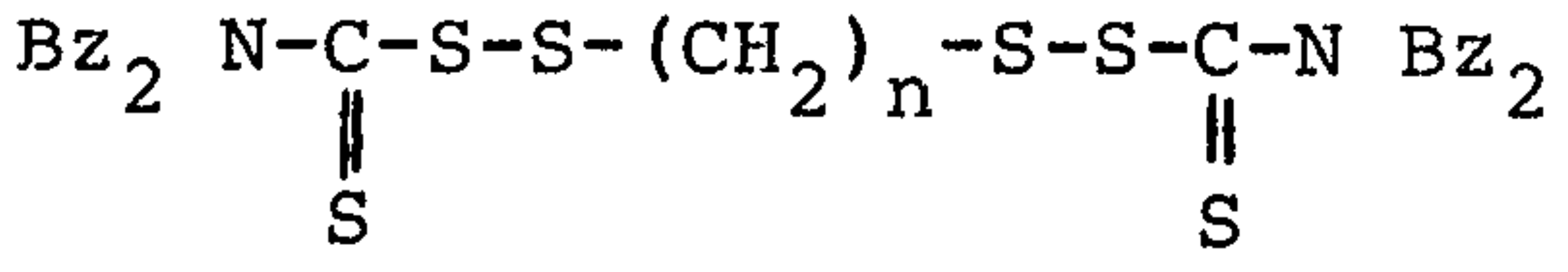
Continuation of Table 4/Base Mixture H:

Recipe		20	21	22	23
Ageing for 14 days at 100 °C					
Tensile strength	MPa	17.9	18	17.1	17.5
Elongation at break	%	424	411	381	446
Modulus at 100% elongation	MPa	3.5	3.6	3.7	3.2
Modulus at 300% elongation	MPa	14.1	14.6	14.8	13.1
Tear strength according to Pohle	N/mm	34	33	32	34
Tension set	%	12	10	10	14
Hardness 22 °C	Shore A	71	72	73	72
Hardness 75 °C	Shore A	60	61	61	60
Elasticity 22 °C	%	35	36	36	35
Elasticity 75 °C	%	47	48	48	46
Compression set 24 h/ 70 °C	%	17	16	16	19
Compression set 24 h/100 °C	%	24	25	23	26
DIN abrasion	mm^3	139	147	156	151
Fatigue test 150 N	°C	104	110	106	106
200 N	°C	134	134	137	144
250 N	°C	160	156	159	167
300 N	°C	187	182	186	194
350 N	°C	7′	11.5′	4′	2′
Goodrich Method 5	°C	57	53	53	57
Deformation	%	-2.5	-2.3	-2.4	-3.3

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for the preparation of a diene rubber vulcanisate having a very high ageing stability and reversion stability, wherein the vulcanisation is carried out at a temperature of from about 140 to about 200°C in the presence of

a) from about 1 to about 4.5 parts of crosslinker substances of the formula I



$$Bz_2N-\underset{\underset{S}{\|}}{C}-S-S-(CH_2)_n-S-S-\underset{\underset{S}{\|}}{C}-NBz_2$$

(I)

wherein n denotes 2 or 6 and Bz denotes benzyl, and

b) from about 0.05 to about 0.3 part of sulphur and

c1) from about 1 to about 2.5 parts of a mercapto accelerator or

c2) from about 0.2 to about 0.8 part of a sulphenamide accelerator or

c3) from about 0.3 to about 2.5 parts of a mercapto accelerator and from about 0.1 to about 0.8 part of a sulphenamide accelerator, relative to 100 parts of diene rubber.

2. A process according to claim 1, wherein

a) from about 2 to about 4 parts of crosslinker substance of the formula I according to claim 1 and

b) from about 0.1 to about 0.2 part of sulphur and

c1) from about 1.3 to about 1.8 parts of a mercapto accelerator or

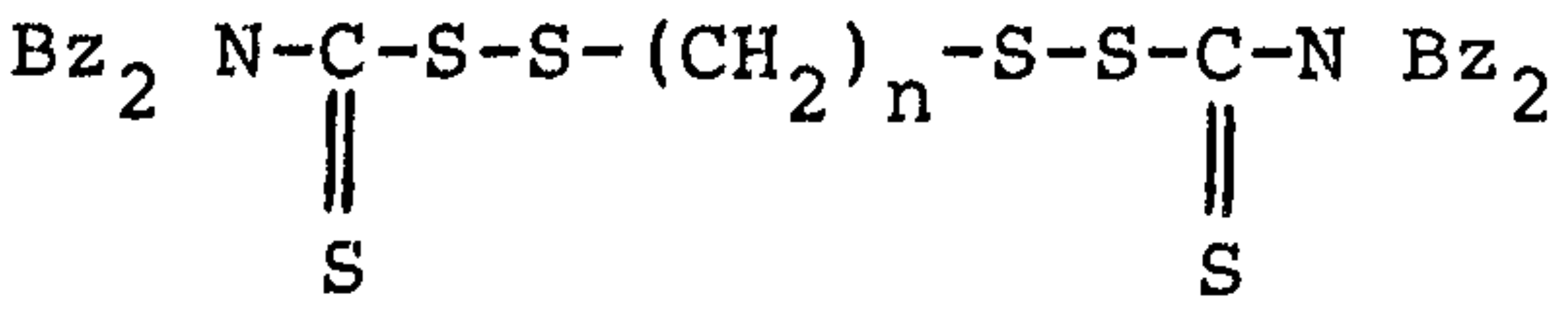
c2) from about 0.3 to about 0.5 part of a sulphenamide accelerator, or c3) from about 0.6 to about 1.5 parts of mercapto accelerator and from about 0.2 to about 0.6 part of sulphenamide accelerator are used per 100 parts of diene rubber.

3. Process according to claim 1 or 2, wherein the diene rubber is selected from the group consisting of natural rubber, cis-polyisoprene, cis-polybutadiene, emulsion SBR, solution SBR, vinyl-polybutadiene, vinyl-SBR, 3,4-polyisoprene, nitrile rubber, polyoctenamer and mixtures thereof.

4. Process according to claim 3, wherein the diene rubber is oil-extended.

5. Use of

a) from about 1 to about 4.5 parts of crosslinker substances of the formula I



$$Bz_2\,N-\underset{\underset{S}{\|}}{C}-S-S-(CH_2)_n-S-S-\underset{\underset{S}{\|}}{C}-N\,Bz_2 \qquad (I)$$

wherein n denotes 2 or 6 and Bz denotes benzyl, and

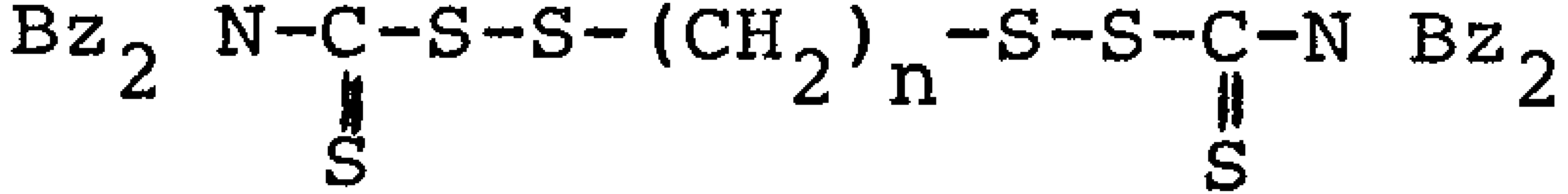
b) from about 0.05 to about 0.3 part of sulphur and

c1) from about 1 to about 2.5 parts of a mercapto accelerator or

c2) from about 0.2 to about 0.8 part of a sulphenamide accelerator or c3) from about 0.3 to about 2.5 parts of a mercapto accelerator and from about 0.1 to about 0.8 part of a sulphenamide accelerator, relative to 100 parts of a diene rubber, for the vulcanisation of the diene rubber.

FETHERSTONHAUGH & CO.
OTTAWA, CANADA

PATENT AGENTS



$$\mathrm{Bz_2\,N-\underset{\underset{S}{\|}}{C}-S-S-(CH_2)_n-S-S-\underset{\underset{S}{\|}}{C}-N\,Bz_2}$$