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Vulcanisation Systems for ENR-50

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This paper compares the effects of cure systems on the physical properties of ENR-50. Semi-EV, EV, 'sulphurless' and some of the newer formulations such as equilibrium cures and post-vulcanisation stabiliser systems have been studied. There is considerable interest currently in vulcanisation systems which do not give rise to volatile nitrosamines and consideration is given to this aspect of selection of vulcanisation systems.

The adjustment of formulations for high temperature curing and injection moulding is also demonstrated. It is shown that ENR-50 may be successfully injection moulded at 180°C and with carefully designed cure systems, compression set similar to that obtained by compression moulding at 150°C can be achieved.

The effects of cure system on the properties of NR are well-established, but comparatively little data has been presented on ENR-50. This paper provides information on cure systems for ENR-50 to assist in the selection of the most suitable cure system for various applications or to meet specifications. The vulcanisation systems were based on some of these evaluated previously for natural rubber[1]. The accelerators, sulphur donors and other constituents of the cure systems used are shown in *Table 1* which gives the abbreviations or trade names and suppliers used.

For the best ageing resistance of ENR-50, cure systems containing more than 1.5 parts p.h.r. sulphur are seldom used[2]. For this reason this investigation was limited to semi-EV and EV systems. Most of these are well known, but some general background observations on the newer systems are appropriate.

Equilibrium cure systems, devised by workers at Degussa[3] for natural rubber give reversion-free cure systems by balancing the loss of modulus on overcure of a sulphur/sulphenamide system by the slow introduction of crosslinks from *SI69* in the presence of accelerator. Wolff showed how to obtain reversion-free systems by correct balance of the sulphur: sulphenamide: *SI69* ratio. A 1:1 mole ratio of *SI69* to sulphenamide is recommended e.g. 3 parts p.h.r. *SI69* to 1.33 parts p.h.r. TBBS and the level of sulphur is then adjusted to give an essentially reversion-free system[4]. The modulus can be adjusted by variation of all three ingredients keeping the ratio of *SI69* : sulphenamide: sulphur constant.

Another interesting development giving improved reversion resistance to natural rubber is the concept of post-vulcanisation stabilisation devised by workers at Monsanto Chemicals[5]. They found that addition of hexamethylene-1, 6-*bis* thiosulphate, disodium salt *(Duralink HTS)* to a conventional cure system resulted in reduced reversion which they attributed to the formation of thermally stable hybrid crosslinks from ruptured polysulphide crosslinks. The hybrid crosslinks formed are said to consist of the more thermally stable hexamethylene group attached to the rubber chains *via* sulphur atoms.

The application of both equilibrium cures and post-vulcanisation stabiliser systems to ENR-50 is investigated, and comparisons are made with some of the more familiar sulphur systems.

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TABLE 1. MATERIALS USED

Abbreviation/Trade name	Chemical name	Supplier
CTP (Santogard PVI)	N-cyclohexylthiophthalimide	Monsanto
DTDM (Sulfasan R)	4,4'-Dithiodimorpholine	Monsanto
Duralink HTS	Hexamethylene-1, 6-bisthiosulphate disodium salt, dihydrate	Monsanto
HPPD (Santoflex 13)	N-1, 3-dimethylbutyl-N'-phenyl-p-phenylenediamine	Monsanto
MBS	N-oxydiethylenebenzothiazole-2-sulphenamide	
MBTS	Dibenzothiazyl disulphide	
OTOS (Cure-Rite 18)	N-oxydiethylene-thiocarbamyl N'-oxydiethylene sulphenamide	BF Goodrich
SI69	Bis-(3-triethoxysilylpropyl)-tetrasulphide	Degussa
TBBS	N-t-Butylbenzolthiazole-2-sulphenamide	
TBTD	Tetrabutylthiuram disulphide	
TMTD	Tetramethylthiuram disulphide	
TMTM	Tetramethylthiuram monosulphide	
TMQ (Flectol Pastilles)	Poly 2,2,3-trimethyl-1,2-dihydroquinoline	Monsanto
ZMMBI (Vulkanox ZMB2)	Zinc 2-mercapto-4 (or 5)-methylbenzimidazole Bayer	Bayer

Until the advent of equilibrium cures and post-vulcanisation stabiliser systems, the best reversion resistance could only be obtained using systems incorporating thiurams. However, there is considerable concern about the levels of nitrosamines, suspected carcinogens formed in minute quantities (parts per billion) in vulcanisates. Stable nitrosamines are only formed from secondary amines, and thiurams are one of the main sources of nitrosamine in the rubber industry *(Figure .1)*. Nitrosamines are also formed from morpholine-containing accelerators, *etc. e.g.* MBS and DTDM. Further examples are given in *Table 1*. Antioxidants containing secondary amines are of little concern as the nitrosamines, if formed, would be involatile.

In semi-EV systems, the choice of sulphenamide for nitrosamine-free systems may easily be restricted to CBS or TBBS, with addition of PVI for improved processing safety. In fast-curing semi-EV systems, or where thiurams are employed in EV systems, the avoidance of nitrosamines is more difficult. The present study utilises TBBS in semi-EV and some EV systems. MBS is used only when other morpholine-containing accelerators are used such as *Sulfasan R* (DTDM) or *Cure-rite 18* (OTOS). Alternatives to thiurams were not investigated.

EXPERIMENTAL

Materials

ENR-50 is Epoxyprene-50 produced by Kumpulan Guthrie Berhad in Malaysia. The accelerators, sulphur donors and other constituents of the cure systems used are shown in *Table 1* which gives the abbreviations or trade names and suppliers used.

Formulations

The basic formulations used are given in *Table 2*. All contained 50 parts p.h.r. N330 HAF black, 5 parts p.h.r. of a high viscosity

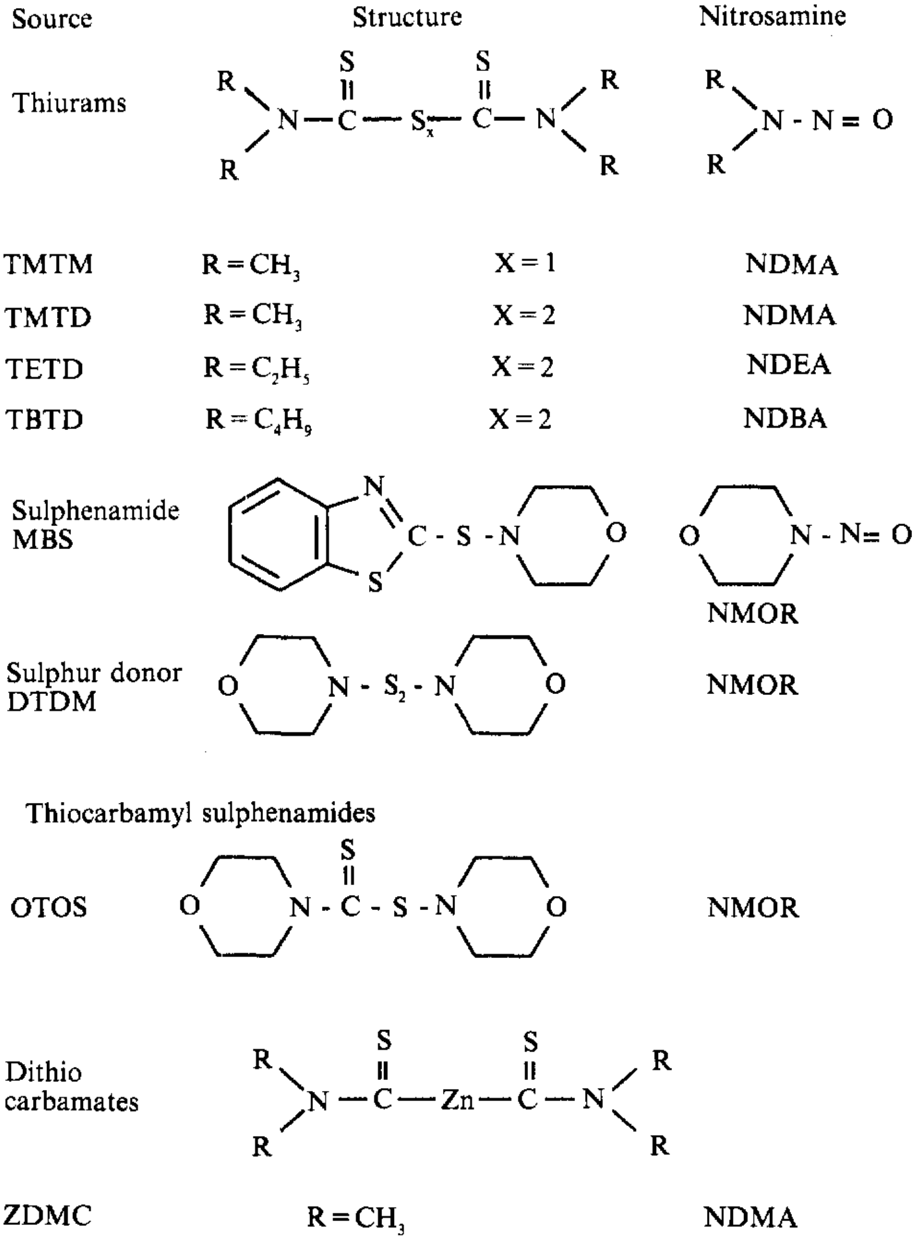

Figure 1. Common sources of nitrosamines.

TABLE 2. BASE FORMULATIONS USED IN THIS STUDY

Compound	Formulation		
	A	B	C
	1	2–9 16–26	10–15
ENR-50	100	100	100
N330 HAF black	50	50	50
Circosol 4240[a]	5	5	5
Calcium stearate	5	5	5
Zinc oxide	5	5	5
Zinc 2-ethylhexanoate	2	–	–
Stearic acid	–	2	2
TMQ	1	1	2
HPPD	2	2	–
Sunproof Improved wax[b]	3	3	–
ZMMBI	–	–	2

[a] High viscosity naphthenic oil (Sun Oils)

[b] Proprietary wax blend (Uniroyal)

naphthenic oil, and 5 parts p.h.r. calcium stearate to improve the ageing characteristics. Most formulations incorporated the zinc oxide/stearic acid activation system but zinc oxide/zinc 2-ethylhexanoate was used for the soluble EV system. The protective systems used were poly-2,2,3-trimethyltetrahydroquinoline (TMQ)/N-dimethylbutyl-N'-phenyl-*p*-phenylenediamine (HPPD) for combined heat ageing and fatigue, or TMQ/zinc salt of methyl mercaptobenzimidazole (ZMMBI) for heat ageing.

In the first part of this study, the TMQ/HPPD protection system was used. The vulcanisation systems incorporated are given in *Table 3*; these include semi- and soluble EV, *Cure-rite 18*, EV and sulphur donor systems, some using no elemental sulphur.

A similar set of cure systems was investigated using the TMQ/ZMMBI protection system, minor adjustments being made, for example to improve the match of moduli between the systems. Formulations are given in *Table 4*.

Formulations illustrating the use of the post-vulcanisation stabiliser *Duralink HTS* are shown in *Table 5* and these utilising equilibrium cure systems are shown in *Table 6*. The TMQ/ZMMBI protection system was used for all of these formulations.

Mix Procedure

Mixing was carried out in a laboratory Banbury using the folowing mix schedule:

Start 60°C, speed 2, cooling water 900 litres/h

0 min	Add rubber + powders
0.75 min	Add half of the black
1.5 min	Add oil and half of the black
3 min	Sweep
4.5 min	Dump

Curatives were added on the mill.

Cure characteristics were assessed on a Monsanto *Rheometer* model 100. Vulcanisates were prepared by compression moulding at 150°C or 180°C and by injection moulding using a *REP B43K* machine at 180°C.

TABLE 3 VULCANISATION SYSTEMS FOR ENR-50 USING TMQ/HPPD PROTECTION SYSTEM

Compound Property	Formulation								
	1	2	3	4	5	6	7	8	9
	A	B	B	B	B	B	B	B	B
Sulphur	0 7	1	0 8	0 5	0 5	0 5	0 3	–	–
TBBS	1 7	2	–	–	2 5	2 4	3 0	–	–
TBTD	0 7	–	–	–	–	–	–	–	–
MBS	–	–	0 55	2 0	–	–	–	1 0	–
OTOS	–	–	1 1	–	–	–	–	–	–
DTDM	–	–	–	1 0	–	–	–	1 0	–
TMTM	–	–	–	–	1 0	–	–	–	–
TMTD	–	–	–	–	–	1 6	2 0	1 0	3 5
MBTS	–	–	–	–	–	–	–	–	0 5
CTP	–	0 2	0 2	–	–	–	–	–	–
Mooney viscosity, 100°C	21	28	30	23	29	29	27	23	25
Scorch 120°C	22	40	34	40	22	12	15	49	23
Rheometer, 150°C									
M_{HR}	27 0	27 5	22	26 5	27 5	31 1	29 2	21	20
t_s1	4 6	7 5	7 0	6 5	5 5	3 0	3 3	10 5	5 2
t_c95	10	13	15	23	22	16	24	39	40
t_c100	15	20	25	35	37	36	50	52	75
Rheometer, 180°C									
M_{HR}	23 0	24 4	17 4	23 1	23 0	26 5	24 6	19 1	17 5
t_s1	1 1	1 5	1 5	1 5	1 5	1 0	1 0	2 7	1 4
t_c95	2 0	2 4	2 9	3 6	3 5	2 8	3 5	5 8	5 6
t_c100	2 6	2 8	3 7	4 3	4 3	3 8	5 0	7 0	8
$t_{5\%}R$	3 9	3 9	5 0	5 6	6 9	8 7	10 2	9 8	>12
Reversion in 6 min, %	14 1	13 5	8 5	7	4 3	2	0	0	0
Cure time, 150°C (min)	20	20	25	35	40	40	40	60	60
Hardness (IRHD)	70	74	70	72	74	74	74	70	67
Lupke resilience (%)	13 1	12 8	13 3	13 6	13 7	13 1	12 8	12 8	13 0
Dunlop resilience, 23°C (%)	21 3	21 7	21 7	22 0	22 6	22 2	22 2	22 6	22 3
Dunlop resilience, 100°C (%)	59 9	61 8	55 5	59 0	62 8	66 1	65 5	54 8	54 7
M100 (MPa)	2 41	2 70	2 18	2 59	2 62	3 06	2 81	2 04	1 94
M300 (MPa)	10 1	11 2	8 35	10 5	11 2	13 9	12 0	8 10	7 68
TS (MPa)	22 2	23 5	21 0	22 0	22 9	22 6	20 0	20 5	21 0
EB (%)	548	547	578	525	521	467	454	594	549
Trouser tear (N/mm)	7 6	10	8 4	10	8	7 5	7 4	7 6	7 7

TABLE 3. VULCANISATION SYSTEMS FOR ENR-50 USING TMQ/HPPD PROTECTION SYSTEM (Contd.)

Compound/Property	Formulation								
	1	2	3	4	5	6	7	8	9
	A	B	B	B	B	B	B	B	B
Compression set (%)									
3 days at 23°C	25	22	24	22	21	20	19	27	27
1 day at 70°C	30	41	38	39	33	31	24	39	37
Ring fatigue, 0%–100%, median (kilocycles to failure)									
Unaged	173	245	465	275	164	129	155	539	610
Aged 7 days/100°C	56	49	112	69	69	40	37	*ca*300	*ca*200
Change of tensile properties aged 3 days at 100°C (%)									
M100	+26	+21	+33	+20	+30	+25	+28	+21	+37
M300	+22	+18	+42	+14	+25	+19	+26	+26	+47
TS	-11	-16	0	-15	-24	-8	-2	-2	0
EB	-14	-19	-11	-13	-30	-20	-18	-13	-15
Change of tensile properties aged 7 days at 100°C (%)									
M100	+68	+49	+68	+34	+43	+56	+54	+37	+49
M300	+46	+32	+61	+18	+30	+27	+40	+28	+64
TS	-26	-28	-19	22	-17	-18	-12	-14	0
EB	-29	37	-36	21	-25	-33	-23	-22	-14
Change of tensile properties aged 14 days at 100°C (%)									
M100	+196	+154	+190	+92	+122	+157	+165	+134	+230
TS	-39	-44	-38	-44	-42	-38	36	-32	-18
EB	-67	-67	-71	-59	-59	-73	-63	-59	-43
Change of tensile properties aged 3 days at 125°C (%)									
M100	+150	+160	+164	+90	+80	+80	+75	+47	+76
TS	-54	-58	-52	-54	-52	-56	-32	-38	-16
EB	-72	-75	-72	-67	-60	-60	-45	-45	-28

A and B = Base formulations.
See *Table 2*.

TABLE 4. VULCANISATION SYSTEMS USING TMQ/ZMMBI PROTECTION SYSTEM

Compound/Property	Formulation					
	10	11	12	13	14	15
	C	C	C	C	C	C
Sulphur	1	0.8	0.5	0.3	–	–
TBBS	2	–	2.4	3.0	–	–
MBS	–	0.55	–	–	1.5	–
OTOS	–	1.1	–	–	–	–
TMTD	–	–	1.6	2.0	1.0	4.0
DTDM	–	–	–	–	1.5	–
MBTS	–	–	–	–	–	0.5
Mooney viscosity, 100°C	28	30	33	31	22	37
Scorch, 120°C	19	10	8	14	46	21
Rheometer, 150°C						
M_{HR}	29	22.5	30.8	30	27	27
t_s1	3.0	2.3	2.0	3.0	8.5	4.0
t_c95	9.0	10.2	12.0	18	32	23
t_c100	16	30	35	50	60	50
Rheometer, 180°C						
M_{HR}	27.4	19.8	28.2	26	24.5	22.5
t_c95	2.2	2.2	2.7	3.4	4.9	4.0
t_c100	2.8	3.6	4.0	5.0	6.5	6.0
Reversion in 6 min (%)	14	4.5	0	0	0	0
Cure time, 150°C (min)	16	30	35	50	60	50
Hardness (IRHD)	69.5	66.5	71.5	70	69.5	66.5
Lüpke resilience (%)	14.6	13.4	13.3	12.8	13.4	13.5
Dunlop resilience (%)	23.6	24.3	25.3	23.6	23.6	25.7
M100 (MPa)	2.64	2.22	2.89	3.10	2.57	2.45
M300 (MPa)	11.2	8.78	13.3	–	10.7	11.3
TS (MPa)	24.8	18.4[a]	23.7	20.2	22.0	23.4
EB (%)	527	502	457	300	504	529
Trouser tear (N/mm)	7.4	6.8	4.7	6.8	5.9	5.8
Compression set (%)						
3 days at 23°C	28	27	17	22	25	21
1 day at 70°C	49	36	25	21	27	26
1 day at 100°C	–	56	35	32	42	36
Ring fatigue, 0%–100%, median life (kilocycles to failure)						
Unaged	175	264	52	57	107	148
Aged 7 days at 100°C	77	114	24	20	59	32
Change of properties on ageing for 7 days at 100°C (%)						
M100	+34	+21	+24	+26	+35	+62
TS	–12	–11	–19	0	–4	–10
EB	–26	+24	–31	–16	–19	–38
Change of properties on ageing for 14 days at 100°C (%)						
M100	+103	+44	–	+45	+40	+80
TS	–48	–21	–60	–8	–12	–10
EB	–60	–32	–60	–21	–26	–36

C = Base formulation

[a] Inconsistent tensile data

See *Table 2*.

TABLE 5 DURALINK HTS IN ENR-50 USING BASE FORMULATION B

Compound/Property	Formulation					
	16		17		18	
Sulphur	1 5		1 5		1 5	
TBBS	1 5		1 5		1 5	
Duralink HTS	–		1 0		2 0	
Mooney viscosity, 100°C	58		55		56	
Scorch, t_5, 125°C	19		15		14	
Rheometer, 150°C						
t_s1	3 5		3 1		3 0	
t_c95	8 5		8 5		12 0	
t_c100	15		25		30	
Reversion in 1 h (%)	8 0		1 7		0 5	
Formulation/Cure	16/1	16/2	17/1	17/2	18/1	18/2
Cure time, 150°C (min)	15	60	15	60	15	60
Hardness (IRHD)	72	70	72	70	72	70
Lupke resilience (%)	13	12	14	12	14	12
M100 (MPa)	3 73	3 16	3 46	3 34	3 69	3 41
M300 (MPa)	14 7	12 8	14 1	13 8	14 6	14 0
TS (MPa)	22 7	20 4	22 0	21 4	23 3	19 6
EB (%)	439	427	445	447	469	407
Compression set (%) 1 day at 70°C	59	32	53	37	45	35
Trouser tear (N/mm)	9 6	5 0	4 5	5 4	4 6	4 6
Ring fatigue life 0%–100% strain median (kilocycles to failure)	88	86	75	76	81	69
Goodrich *Flexometer*, 10 88 kg load, 5 71 mm stroke, 30 Hz, start 23°C 30 min duration						
Temperature rise (°C)	65	70	60	62	61	59
Change of properties aged 3 days at 100°C (%)						
M100	+24	+40	+35	+30	+45	+50
M300	+17	+26	+90	–	–	–
TS	–14	–10	–16	–24	–33	–34
EB	–22	–20	–27	–23	–46	–50

RESULTS AND DISCUSSION

Semi-EV and EV Systems; TMQ/HPPD Protection System

Formulations and properties are recorded in *Table 3*

The processing safety of these formulations, assessed by Mooney scorch at 120°C, was generally high, particularly for those systems containing the pre-vulcanisation inhibitor Two of the low elemental sulphur EV systems, *Formulations 6* and *7*, possessed rather low processing safety, but this is common with this type of formulation containing TMTD. A similar formulation containing TMTM, *Formulation 5*, gave considerably improved processing safety.

TABLE 6. EQUILIBRIUM CURE SYSTEMS IN ENR-50 USING BASE FORMULATION B

Compound/Property	Formulation			
	19		20	
Sulphur	0.6		0.8	
TBBS	1.33		1.33	
SI69	3.0		3.0	
Mooney viscosity, 100°C	47		41	
Scorch, t_5, 120°C	38		37	
Rheometer, 150°C				
t_s1	7.2		6.5	
t_c95	19		17	
t_c100	40		37	
Reversion in 2 h (%)	5.0		7.0	
Formulation/Cure	19/1	19/2	20/1	20/2
Cure time, 150°C (min)	40	85	40	85
Hardness (IRHD)	66	65.5	68	69.5
Lüpke resilience (%)	18	18	16	15
M100 (MPa)	2.27	2.30	2.55	2.62
M300 (MPa)	9.12	8.62	9.80	10.1
TS (MPa)	20.0	16.3	18.7	18.2
EB (MPa)	529	477	502	472
Compression set 1 day at 70°C (%)	44	41	46	40
Trouser tear (N/mm)	5.5	5.8	5.8	6.1
Ring fatigue life, 0%–100% strain, median (kilocycles to failure)	270	480	167	255
Goodrich *Flexometer*, 10.88 kg load, 5.71 mm stroke, 30 Hz, start 23°C, 30 min duration				
Temperature rise (°C)	118	113	112	107
Change of properties aged 3 days at 100°C (%)				
M100	+57	+50	+62	+60
M300	+47	+45	+54	+50
TS	−7	+2	−3	−2
EB	−23	−20	−30	−26
Change of properties aged 7 days at 100°C (%)				
M100	+178	+150	+224	+170
TS	−30	−18	−36	−38
EB	−60	−60	−70	−70

The soluble EV, semi-EV, OTOS and EV formulations *(Nos. 1–6)* were fast curing at 150°C and 180°C, whereas the two sulphurless systems (*Formulations 8* and *9*) were slowest curing and together with *Formulation 7* showed least reversion. Of the other EV systems, reversion at 180°C increased almost in proportion to the level of elemental sulphur added. However, the soluble EV system was an exception as it showed no greater reversion resistance than the semi-EV system at 180°C.

Test pieces were cured approximately to *Rheometer* t_{max} at 150°C. There were considerable differences in hardness and moduli among these formulations; for example hardness varied between 67 IRHD and 74 IRHD and M100 varied from 1.9 MPa to 3.1 MPa. The lowest hardness and modulus were obtained by the 'sulphurless' TMTD *Formulation 9* and highest from the EV *Formulation 6*. These differences in moduli must be recognised when considering other properties which are known to be modulus-dependent, particularly fatigue life.

The tensile strength and elongation at break of these ENR formulations are broadly similar to those of NR in similar formulations, although tear strengths are somewhat lower.

Very low resilience at 23°C was obtained with all of these formulations, with no effect of modulus because of the relatively high T_g of ENR-50 (–25°C). However, results measured at 100°C were substantially higher and there was a reasonable correlation between Dunlop resilience at 100°C and M100. Because of the very low resilience of ENR-50 at ambient temperature it may find applications in, for example, vibration damping systems which operate at, or close to resonance conditions. However, the proximity of the glass transition temperature of this polymer to ambient temperature resulted in substantial changes in resilience and modulus with temperature and frequency. This must be considered in any application of ENR-50 as substantial temperature rise within a component could occur if deformed at high frequencies and/or high strains. Applications as an energy absorbing material are more appropriate to conditions where heat generation will not be excessive *i.e.* low strains, *e.g.* in acoustic damping.

The compression set of these vulcanisates was somewhat higher than those of similar NR vulcanisates. The lowest set at 70°C was obtained with *Formulation 7*, a high modulus EV system. The low-moduli sulphurless EV *Formulations 8* and *9* showed no advantage in compression set over the semi-EV *Formulation 2*. Some improvement in compression set was obtained with *Formulations 1, 5* and *6*, soluble EV and EV systems.

The fatigue lives of all rubbers are highly dependent on crosslink density and the large difference in moduli between these formulations makes comparisons between systems difficult. After allowing for moduli effects, the present data show that the fatigue lives of the semi-EV and DTDM systems, *Formulations 2* and *4*, may be somewhat greater than those of the EV systems of similar moduli, *Formulations 1* and *5*. After ageing for seven days at 100°C, the EV systems, particularly *Formulation 8*, showed somewhat lower change in fatigue lives.

An EV system of somewhat lower crosslink density may sometimes be acceptable because of the difficulty in obtaining high fatigue lives in EV vulcanisates. Alternatively, the modulus may be increased by increasing the filler loading for the EV system, but this could have detrimental effects on other properties, *e.g.* heat build-up.

After ageing for three and seven days at 100°C, the sulphurless and the very low sulphur EV systems (*Formulations 8, 9* and *7*) showed the least change of tensile strength. However, the soluble EV system showed no advantage over the semi-EV system. Under more extreme conditions of ageing, the sulphurless TMTD system showed greatest ageing resistance.

Semi-EV and EV Systems; TMQ/ZMMBI Protection System

A similar set of formulations was investigated using the TMQ/ZMMBI protection system as shown in *Table 4*. However, some adjustments were made to the two sulphurless formulations of lowest moduli in order to obtain a closer match of properties. In addition, the pre-vulcanisation inhibitor was not used as the processing safety of these formulations was adequate. Apart from these changes, the processing safety of these formulations were broadly similar to those of the previous mixes. Vulcanisation characteristics were also similar.

The hardness of these formulations ranged from 67 IRHD to 72 IRHD, somewhat lower than that of the previous set of formulations. The M100 varied from 2.2 MPa to 3.1 MPa, those of the two sulphurless formulations whose curative levels were adjusted were now 2.6 MPa and 2.5 MPa, a very good match to that of the semi-EV system. For the formulations whose cure systems were unchanged, the moduli were well matched to those of the corresponding formulations in the previous set.

The changes in formulation of the 'sulphurless' EV system resulted in substantial improvements in compression set. However, *Formulation 13* whose cure system was identical to that of *Formulation 7* possessed the lowest compression set.

The fatigue lives of *Formulations 10–15* were less than those of *Formulations 1–9* as the former contained no anti-flex cracking agent. The reduction in fatigue life was about 30% for the semi-EV *Formulation 10*, compared with 40%–50% for those EV systems with no change in composition. As expected, the greatest reduction in fatigue lives occurred for those systems of increased crosslink density. The EV *Formulation 14* appeared to give the best retention of fatigue life on ageing, which is consistent with earlier findings.

When protected with TMQ/ZMMBI the change of tensile properties on ageing for seven days at 100°C for the semi-EV *Formulation 10* was as low as that of some of the EV systems, although after longer term ageing the advantages of the EV systems were more apparent. The best ageing characteristics were obtained by the EV *Formulation 13* and the 'sulphurless' EV *System 14* and *15*. These observations are broadly similar in ranking to those observed above. The EV *Formulation 12* appeared to age significantly more than the other systems in the TMQ/ZMMBI system, a feature not observed in the earlier work.

Post-vulcanisation Stabilisation Systems

Post-vulcanisation stabilisers are effective as a method of reducing the reversion of high sulphur NR systems, and are of interest in semi-EV ENR if they also reduce reversion. A semi-EV formulation with equal levels of sulphur and accelerator was used as a control. *Duralink HTS* was added at 1 part and 2 parts p.h.r. *(Table 5)*.

Marginal reductions in processing safety were observed, both measured by Mooney scorch at 120°C and *Rheometer* scorch at 150°C. The addition of 1 part p.h.r. *Duralink* had no effect on the time to *Rheometer* t_c95, but the higher level resulted in a 50% increase in t_c95. The time to maximum *Rheometer* torque, t_c100, increased substantially for both formulations containing *Duralink* and reversion in 1 h was reduced to trivial levels. The rheographs are shown in *Figure 2*. These demonstrate that there is a reduction in cure rate in the latter part of the graph, and that the maximum torque is decreased by *Duralink* addition. Test pieces were cured for 15 min and 60 min for each mix. This is equivalent to the maximum *Rheometer* torque for the semi-EV control formulation and a four-fold overcure.

The hardness of all formulations for the 15 min cure was 72 IRHD and 70 IRHD on extended cure, so *Duralink* had no effect on hardness. The M100 for the shorter cure time varied from 3.5 MPa to 3.7 MPa, so

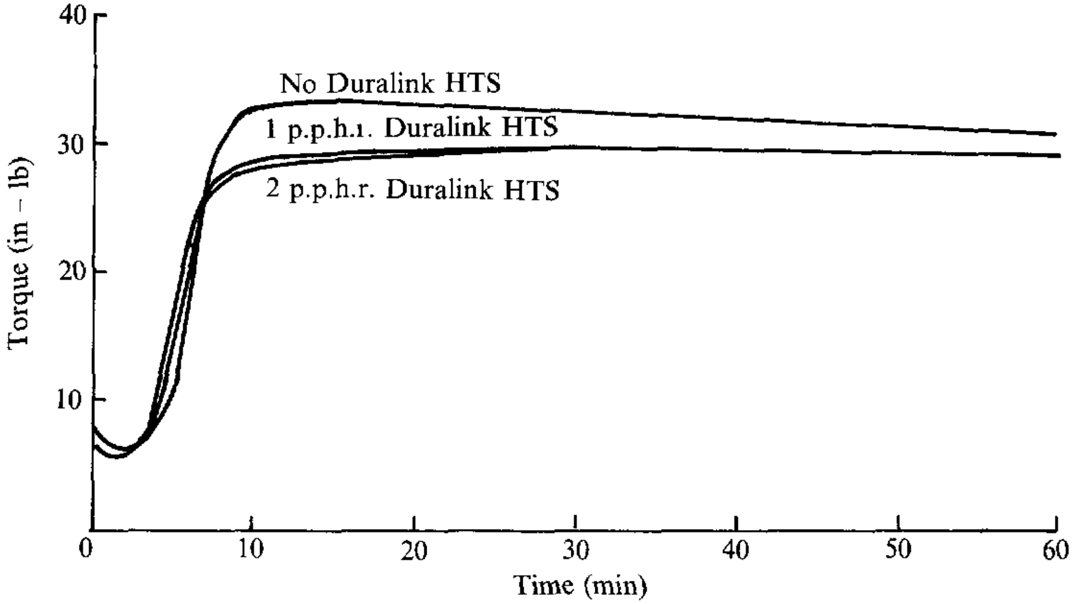

Figure 2. Effect of Duralink HTS on the cure characteristics of ENR-50 at 150°C using a semi-EV system.

Duralink had little effect on moduli. The control formulation showed a 15% decrease in modulus on overcure, whereas those containing *Duralink* showed only 2%–8% decrease. The tensile strength and elongation at break for the shorter cure times were also unaffected by *Duralink*. However, on overcure the formulation containing 1 part p.h.r. of *Duralink* showed marginally better tensile properties. By contrast at 2 parts p.h.r. *Duralink*, the tensile properties were marginally inferior on overcure.

There was a marginal improvement in compression set with increasing *Duralink* level for the shorter cure time, which is rather surprising as the test pieces are, in effect, progressively undercured as they were cured to original cure time for the control without *Duralink*. On overcure there was no significant difference between any of these formulations.

The tear strengths of the formulations containing *Duralink* were less than that of the control at the short cure time, but on extended cure there was no significant difference.

The differences in fatigue lives observed were not really significant. Overall, the lives were low for semi-EV formulations, a reflection of the high moduli.

Minor reductions in heat build-up on the Goodrich *Flexometer* were observed for formulations containing *Duralink*, particularly on extended cure.

On ageing for three days at 100°C, the formulations containing *Duralink* showed inferior performance to the semi-EV control for both cure times.

There was no real advantage in using more than 1 part p.h.r. *Duralink* in the cure system studied.

Equilibrium Cure Systems

Two attempts to devise equilibrium cure systems for carbon black-filled ENR-50 are shown in *Table 6*. They utilise a 1:1 mole ratio of *SI69* to TBBS with differring levels of sulphur in an attempt to achieve a reversion-free system. The rheometer traces are shown *in Figure 3* and *demonstrate that* minor reversion was apparent after about 40 min at 150°C. For a completely reversion-free system, a somewhat lower sulphur level would be required. However, the modulus would then be lower. Additional *SI69* and other curatives could be used to off-set this, but costs would be higher. The times to *Rheometer* t_c95 for these formulations are reasonably low for reversion-resistant formulations and processing safety is very good.

Test pieces were cured for 40 min, which corresponded to rheometer maximum torque, and a standard overcure of 85 min at 150°C.

The formulations showed excellent maintenance of hardness and modulus on overcure, although ultimate tensile properties were reduced somewhat.

The compression set of these formulations were comparable with those obtained earlier for semi-EV systems; minor improvements being observed for the longer cure time.

The fatigue lives of these formulations cured to maximum torque are reasonably in accord with those of semi-EV and EV systems shown in *Table 3*, where moduli are *similar*. However, *on overcure substantial* increases in fatigue lives are observed, a feature not observed with other systems.

On ageing for seven days at 100°C, the tensile ageing characteristics were all somewhat inferior to those observed of the semi-EV *Formulation 2*, although the shorter ageing period showed somewhat less reduction in tensile strength.

High Temperature Vulcanisation

When vulcanising rubbers at high temperature, the cure systems must be adjusted to compensate for the decrease in modulus, due to the decrease in crosslink density, which occurs on raising the temperature of vulcanisation. In most cases, an increase in sulphur and accelerator levels of about 20%, is sufficient for vulcanisation at about 180°C. However, processing safety may be impaired and this may require further adjustments in the formulation to obtain the desired modulus and cure time with appropriate processing safety.

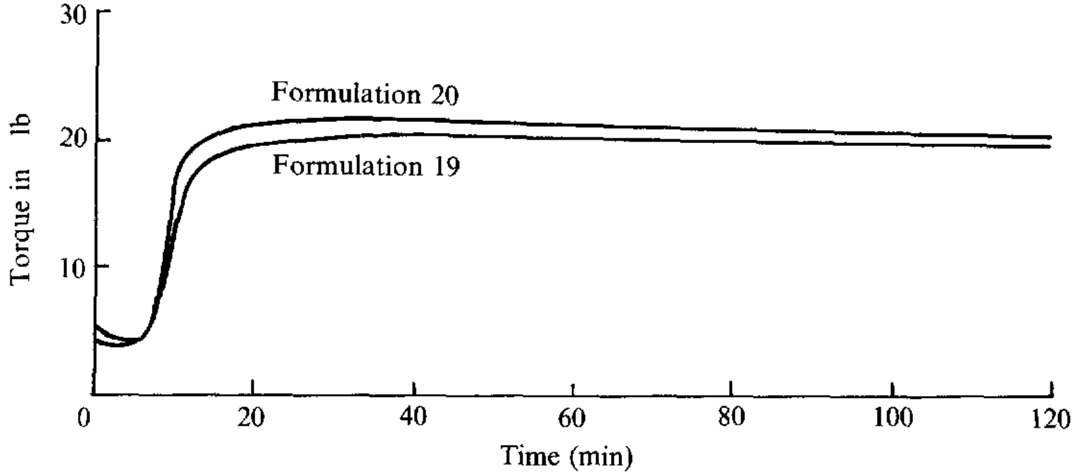

Figure 3. Cure characteristics of ENR-50 using equilibrium cure systems at 150°C.

Table 7 shows six modified EV formulations in an attempt to achieve a reasonable level of modulus at a cure of 180°C. All are based on *Formulation B (Table 1)*. *Formulation 21* is identical to that of *Formulation 6* in *Table 3*, as this gave a high modulus so only minor adjustments to curative levels were made in *Formulation 22*. *Formulations 23* and *24* are low sulphur/high sulphenamide EV systems which do not contain any thiurams. *Formulations 25* and *26* are sulphurless systems based on those of *Formulations 8*

TABLE 7. EV SYSTEMS USING BASE FORMULATION B

Compound/Property	Formulation 21	22	23	24	25	26
Sulphur	0.5	0.6	0.4	0.5	–	–
TBBS	2.4	2.9	–	–	–	–
CBS	–	–	6.0	6.0	–	–
MOR	–	–	–	–	1.5	–
TMTD	1.6	1.9	–	–	1.0	5
DTDM	–	–	–	–	1.5	–
MBTS	–	–	–	–	–	1
Rheological properties						
Mooney viscosity 100°C	40	39	42	42	41	42
Mooney scorch, 120°C	14	12	15	14	27	10
Rheometer, 180°C						
M_{HR}	27.0	29.5	21.5	23.0	24.0	23.5
t_c95	3.0	2.9	3.4	3.2	6.3	5.0
t_c100	3.8	3.8	4.3	4.2	7.3	7.0
Reversion in 12 min (%)	10	9	8.1	8.5	11.0	3.4

Vulcanisate properties – compression moulded

No	Vulcanisation conditions (min °C)	Unaged M100 (MPa)	Unaged M300 (MPa)	Unaged TS (MPa)	Unaged EB (%)	Change after ageing for 7 days at 100°C (%) M100	TS	EB
21/1	4.0/180	2.93	13.6	22.3	459	+83	–37	–55
21/2	3.5/180	2.95	13.9	22.8	450	+86	–40	–58
21/3	3.0/180	3.02	14.1	22.7	448	+97	–30	–50
22/1	4.0/180	3.29	15.1	21.7	411	+89	–33	–54
22/2	3.5/180	3.37	15.1	19.7	375	+90	–23	–50
22/3	3.0/180	3.42	14.8	19.5	379	+75	–30	–50
23/1	4.0/180	2.08	8.40	20.1	525	+22	–38	–32
23/2	3.5/180	2.06	8.20	18.0	492	+30	–33	–30
23/3	3.0/180	1.93	7.76	20.7	550	+44	–37	–36
23/4	2.5/180	1.71	6.88	18.0	557	+62	–30	–36
24/1	4.0/180	2.23	9.00	19.6	540	+28	–35	–35
24/2	3.5/180	2.26	9.22	20.3	514	+34	–40	–36
24/3	3.0/180	2.08	8.53	18.5	530	+47	–27	–43
24/4	2.5/180	2.02	8.28	20.2	552	+53	–40	–45
25/1	7.0/180	2.08	9.22	20.5	495	+70	–32	–40
26/1	7.0/180	2.07	8.77	19.0	490	+71	–18	–32

and *9* with adjustments in an attempt to increase the moduli. No increase in thiuram was made in an attempt to maintain good processing safety.

Formulations 21–24 were all fast curing at 180°C with reasonable processing safety The sulphurless formulations were the slowest curing while that containing DTDM had the greatest processing safety but the least reversion resistance.

These formulations were compression moulded at 180°C in a fast-acting press. The results are given in *Table 7*. *Formulations 21* and *22* both gave high moduli; moduli of the latter being higher than that of the original *Formulation 6*. *Formulation 23* gave rather low moduli, but that of *Formulation 24* was somewhat improved. The two sulphurless systems also gave rather low moduli

The best ageing resistance was obtained with the 'sulphurless' TMTD system The ageing resistance of these mixes were not as good as those observed earlier, cured at 150°C, even for mixes of identical formulation (of *Mixes 21* and *6*).

Thus, in order to match the performance of the product cured at lower temperatures, it may be necessary to change to a more efficient vulcanisation system, as well as modify the formulation to compensate for the decrease in crosslink density.

TABLE 8 FORMULATIONS FOR INJECTION MOULDING

Formulation			
ENR-50	100		
HAF N330	50		
Circosol 4240	5		
Calcium stearate	5		
Zinc oxide	5		
Stearic acid	2		
HPPD	3		
TMQ	1		
Wax blend	3		
		Formulation	
	27	28	29
Sulphur	1 8	1 2	0 5
TBBS	1 8	2 4	4 2
TMTD	–	–	0 8
Rheological properties			
Mooney viscosity, 100°C	35	35	34
Mooney scorch, 120°C	20	24	14
Rheometer, 180°C			
M_{HR}	26 0	26 5	26 6
t_s1	1 0	1 1	1 1
t_c95	1 95	2 1	3 4
t_c100	2 2	2 4	4 4
Reversion in 6 min (%)	21	15	5

Injection Moulding

Injection moulding trials were carried out using three formulations, two semi-EV and one EV as shown in *Table 8*. The EV system chosen was a hybrid of *Formulations 21* and *24*.

Injection moulding trials were carried out using a *REP B43K* machine using the following machine settings:

Screw temperature	75°C
Ram chamber temperature	100°C
Nozzle block temperature	80°C
Nozzle diameter	3.5 mm
Injection temperature	120°C
Injection time	3–4 s
Mould temperature	180°C

There was some tendency for the mixes to stick to the partially-filled extruder screw but this can be overcome by the use of about 3–5 parts p.h.r. of a zinc soap process aid such as *Struktol A60* or equivalent material.

Tensile and ring fatigue measurements were made on 2 mm and 1 mm sheets, respectively, moulded in a centre-gated mould using vulcanisation times up to *Rheometer* t_c100. Hardness, resilience and compression set test pieces were moulded in a multi-cavity mould using times from *Rheometer* t_c95 to in excess of 6 min in order to assess the influence of vulcanisation time on the properties of thicker mouldings. Compression set measurements were made on two different test pieces: *Type A* were

TABLE 9. INJECTION MOULDED VULCANISATES FROM FORMULATION 27

Property	Vulcanisate				
	27/1	27/2	27/3	27/4	
1 mm and 2mm thick sheets					
Vulcanisation time (min)	0.9	1.4	1.9	2.2	
Tensile properties, measured radially					
M100 (MPa)	2.03	1.99	2.05	2.00	
M300 (MPa)	7.95	8.02	8.33	7.85	
TS (MPa)	22.9	22.2	22.0	18.7	
EB (%)	563	541	546	494	
Tensile properties, measured tangentially					
M100 (MPa)	2.34	–	2.18	–	
M300 (MPa)	10.0	–	8.81	–	
TS (MPa)	24.5	–	21.6	–	
EB (%)	565	–	558	–	
Ring fatigue life, 0%–100% extension (kc to failure)	98	–	43	–	
	Vulcanisate				
	27/4	27/5	27/6	27/7	27/8
Thicker specimens					
Vulcanisation time (min)	2.2	3.0	4.0	5.0	6.0
Hardness (IRHD)	65	64	62	61	60
Lüpke resilience (%)	–	20	18	17	16
Compression set (%)					
1 day at 70°C	64	56	51	49	46

13 mm diameter and 6.3 mm thick; *Type B* were 29 mm diameter and 12.5 mm thick.

The two semi-EV systems gave good processing safety and were fast curing. Some improvements in reversion resistance were observed with the lower sulphur level. The EV system had slower vulcanisation characteristics and lower processing safety.

The moduli and tensile properties of the high-sulphur semi-EV system (*Formulation 27, Table 9*) were almost independent of vulcanisation time from 1–2.2 min whereas *Formulation 28, Table 10* showed a wider range over vulcanisation times of 0.75–2.5 min. The EV *Formulation 29, Table 11* also gave reasonably constant moduli over a wide range of cure times.

Anisotrophy was assessed by measurement of moduli and tensile strength along radial and tangential directions of the

TABLE 10. INJECTION MOULDED VULCANISATES FROM FORMULATION 28

Property	Vulcanisate					
	28/1	28/2	28/3	28/4	28/5	
1 mm and 2 mm sheets						
Vulcanisation time (min)	0.75	1.1	1.6	2.1	2.5	
Tensile properties, measured radially						
M100 (MPa)	1.94	2.13	2.09	2.05	2.06	
M300 (MPa)	7.59	8.88	8.68	8.43	8.48	
TS (MPa)	23.8	23.6	23.1	22.8	23.0	
EB (%)	587	540	543	533	549	
Tensile properties, measured tangentially						
M100 (MPa)	–	2.56	–	2.46	–	
M300 (MPa)	–	11.4	–	11.1	–	
TS (MPa)	–	24.0	–	24.2	–	
EB (%)	–	524	–	535	–	
Ring fatigue life, 0%–100% extension (*kc to failure*)	–	88	–	77	–	
Change in tensile properties after air-oven ageing for 3 days at 100°C						
M100 (%)	+44	+45	+41	+43	+35	
TS (%)	–16	–32	–30	–37	–28	
EB (%)	–25	–33	–34	–38	–30	
Thicker specimens	28/4	28/5	28/6	28/7	28/8	28/9
Vulcanisation time (min)	2.1	2.5	3.0	3.5	4.0	5.0
Hardness (IRHD)	–	63	63	63	62	61
Lüpke resilience	–	–	22	19	19	18
Compression set (%)						
Type A, 1 day at 70°C	28	26	26	25	24	24
Type B, 1 day at 70°C	–	–	34	29	28	25

TABLE 11. INJECTION MOULDED VULCANISATES FROM FORMULATION 29

Property			Vulcanisate			
	29/1	29/2	29/3	29/4	29/5	
1 mm and 2 mm sheets						
Vulcanisation time (min)	1.9	2.4	2.9	3.5	4.3	
Tensile properties, measured radially						
M100 (MPa)	1.85	2.11	2.13	2.04	2.06	
M300 (MPa)	8.15	9.06	9.39	8.99	9.11	
TS (MPa)	21.2	23.0	23.4	21.0	21.7	
EB (%)	526	522	520	495	500	
Tensile properties, measured tangentially						
M100 (MPa)	–	2.39	–	2.54	–	
M300 (MPa)	–	11.2	–	12.1	–	
TS (MPa)	–	22.7	–	23.3	–	
EB (%)	–	490	–	490	–	
Ring fatigue life, 0%–100% extension, (kc to failure)	–	62	–	36	–	
Change in tensile properties after air-oven ageing for 3 days at 100°C						
M100 (%)	+85	+100	+39	+30	+26	
TS (%)	–15	–33	–24	–20	–25	
EB (%)	–40	–44	–30	–24	–20	
Change in tensile properties after air-oven ageing for 7 days at 100°C						
M100(%)	+110	+76	+70	+66	+60	
TS (%)	–36	–42	–44	–50	–44	
EB (%)	–54	–53	–52	–55	–50	
			Vulcanisate			
Thicker specimens	3/4	3/5	3/6	3/7	3/8	3/9
Vulcanisation time (min)	3.5	4.0	5.0	6.0	7.5	9.0
Hardness (IRHD)	62	63	62	62	61	60
Lüpke resilience (%)	18	18	18	18	17	17
Compression set (%)						
Type A, 1 day at 70°C	22	22	22	22	23	24
Type B, 1 day at 70°C	25	25	21	20	19	20

centre-gated sheets. Averaged over all the vulcanisation systems and vulcanisation times, M100 and M300 measured tangentially were 15% and 22% higher than when measured in the radial direction. Anisotrophy in tensile strength and elongation at break were negligible.

Hardness measurements were made on *Type B* compression set test pieces.

Formulations 27 and *28* gave no porosity when vulcanised to *Rheometer* t_c95. Lüpke resilience test pieces (65 mm diameter, 12.5 mm thick) required an extra 0.5 min for porosity-free moulding.

Compression set measurements showed the anticipated reduction in set with sulphur level, as well as a reduction in set with increasing vulcanisation time. For the small *Type A* test pieces, acceptable results could be obtained with reasonably short vulcanisation times, but for the larger *Type B* test pieces, the best results were obtained by vulcanising to at least *Rheometer* t_c100 + 0.5 min. At optimum cure, there was no difference in set between the two types of test pieces, and the best results were broadly similar to those obtained by compression moulding at 150°C.

The ageing resistance of those injection moulded formulations were inferior to those of similar formulations compression moulded at 150°C, but generally similar to those compression moulded at 180°C.

CONCLUSIONS

This paper demonstrates how to select a cure system for ENR-50 and how the properties may be varied. This should aid compounders in their selection of the most appropriate formulations for a particular application. To further this aim, the following brief resume of the attributes of each cure system is given (based on vulcanisation at 150°C) compared to the general-purpose semi-EV formulation.

Semi-EV

1 S/2 TBBS (p.p.h.r.)	Fast curing, adequate processing safety, secondary amine-free, general purpose.

EV systems containing volatile secondary amines

0.8 S/ 0.55 MBS/ 1.1 OTOS	Fast curing, improved reversion resistance, moderate ageing resistance, good fatigue resistance.
0.7 S/ 1.4 TBBS/ 0.7 TBTD (Soluble EV)	Fast curing, no improvement in reversion or ageing resistance, compared to semi-EV, non-blooming.
0.5 S/ 2.0 MBS/ 1.0 DTDM	High processing safety, improved reversion resistance, moderate ageing resistance.
0.5 S/ 2.5 TBBS/ 1.0 TMTM	Good reversion resistance, reduced fatigue life, improved ageing resistance.
0.5 S/ 2.4 TBBS/ 1.6 TMTD	Low processing safety, fast curing for EV system, excellent reversion resistance, high modulus, poor fatigue life, good ageing performance.
0.3 S/ 3.0 TBBS/ 2.0 TMTD	Low processing safety, very good reversion resistance, high modulus, lowest compression set, low fatigue life excellent ageing resistance.

'Sulphurless' EV systems containing volatile secondary amines

1.0 MBS/ 1.0 DTDM/ 1.0 TMTD	High processing safety, slow curing, highest reversion resistance, low modulus, poor compression set, high fatigue life, good ageing performance.
1.5 MBS/ 1.5 DTDM/ 1.0 TMTD	High processing safety, slow curing, high reversion resistance, higher modulus, improved compression set, lower fatigue life.
3.5 TMTD/ 0.5 MBTS	Slow curing, reasonable processing safety, highest reversion resistance, low modulus, poor compression set, high fatigue life, best ageing performance.
4.0 TMTD/ 0.5 MBTS	Slow curing, reasonable processing safety, highest reversion resistance, higher modulus, improved compression set, lower fatigue life, very good ageing performance.

Reversion resistant systems free of volatile secondary amines

Duralink HTS	Improved reversion resistant and maintenance of properties on extended curing, reduced ageing performance. Little or no improvement in compression set over semi-EV. Secondary amine-free (if CBS or TBBS are used).
Equilibrium cure systems	Excellent processing safety, good reversion resistance and maintenance of properties on extended curing. No improvement in compression set and ageing performance over semi-EV. High fatigue life (but modulus low). Increase in fatigue life on overcure. Secondary amine-free (if CBS or TBBS are used).

These effects are broadly similar to those established for NR.

An investigation of cure systems for high temperature curing showed the expected reduction in modulus. However, by appropriate adjustment of the curative levels, formulations of reasonable moduli and cure rates were obtained. It was also shown that heat ageing resistance decreases when the temperature of curing is raised from 150°C to 180°C. Hence, it may be desirable to use a more efficient cure system for curing at high temperature than would be used for curing at 150°C.

Data is also presented for injection moulding trials on three formulations; two fast curing semi-EV systems and one EV system. Sheets of 2 mm thick were successfully injection moulded with cure times from 0.75 min to 4 min at 180°C. Thicker specimens required longer cure times, particularly in order to obtain the lowest compression set. However, the best compression set results for the EV system were comparable to, or better than, those obtained for the best EV system when cured at 150°C *(cf Table 3)*.

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