Structural Requirements for NR Vulcanisates with Improved Flex Resistance after ageing

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For some time, rubber compounders have been confronted with the enigmatic situation that vulcanisates containing polysulphidic cross-links, while possessing superior initial resistance to tensile and fatigue failure, show relatively poorer retention of these properties during thermal or thermo-oxidative ageing. On the other hand, vulcanisates containing monosulphidic cross-links, with somewhat inferior initial tensile and fatigue properties when relaxed through zero strain, show excellent retention of these properties during ageing.

The precise manner in which sulphur is incorporated in the network seems to be a key factor regarding the retention of tensile strength and fatigue properties during ageing. Inefficient use of sulphur in main-chain modifications leads, during thermal ageing, to more rapid deterioration in fatigue properties.

These points are illustrated in this paper by reference to different network structures. In addition, the use of dimorpholino disulphide as a partial replacement for elemental sulphur to obtain practical vulcanisates combining good initial fatigue properties with improved retention of these properties during ageing, is examined in detail.

The rupture of natural rubber gum and filled vulcanisates during tensile, cut-growth or fatigue tests is known to be dependent upon the type of cross-links they contain. That the order of increasing tensile strengths, $-C-C- < -C-S-C- < -C-S_x-C-$, is the reverse of chemical bond strengths has been rationalised (COOPER, 1955 and 1958; DOGADKIN *et al.*, 1963; BATEMAN *et al.*, 1963a) in terms of a stress-induced rearrangement of labile polysulphidic cross-links to relieve localised high stress concentrations. Similar correlations of fatigue performance with vulcanisate structure are less clearly defined, possibly because of past difficulties in the generation of meaningful fatigue failure data. Nevertheless, conventional vulcanisates of an essentially polysulphidic character are generally claimed (BEATTY, 1964; COX AND PARKS, 1966) to give a performance superior to those of a monosulphidic nature prepared in the absence of elemental sulphur when the test samples are relaxed through zero strain.

Two recent developments, both from the laboratories of the Natural Rubber Producers' Research Association, enable these empirical relationships to be subjected to closer scrutiny. Improved analytical methods (BATEMAN, *et al.*, 1963b; SAVILLE AND WATSON, 1967; PORTER, 1967) now enable the structures of vulcanisates to be more precisely determined than in the past. Furthermore, the rate of cut-growth in a rubber sample, or in the ultimate, its flex or fatigue life, measured in cycles to failure, has been shown (GENT *et al.*, 1964; LAKE AND LINDLEY, 1964a and b) to be dependent upon the tearing energy dissipated by the growth of the cut, which in turn is related to the strain energy per unit volume in the sample. In contrast with earlier methods, this approach enables the cut-growth characteristics or fatigue lives of vulcanisates of different moduli to be compared directly. By employing this technique the superior cut-growth resistance of vulcanisates with polysulphidic cross-links, compared with those containing more rigid carbon-carbon cross-links, can be readily demonstrated.

In the Monsanto laboratories (LLOYD, 1968),

the fatigue lives of stocks derived from several vulcanisation systems known to give either essentially monosulphidic or polysulphidic cross-links *(Table 1)* have been compared by this N.R.P.R.A. method on a strain-energy basis. The results depicted graphically in *Figure 1* show that the difference in fatigue behaviour between stocks depends upon the type of cross-link produced during cure rather than on the vulcanisation system used to produce the cross-link. Earlier reports of the superior performance of the polysulphidically

cross-linked vulcanisates when relaxed through zero strain, are confirmed. Even with the most efficient anti-oxidant systems present, it is not possible to raise the performance level of the monosulphidic vulcanisate to that of the unprotected polysulphidic stock *(Figure 2)*.
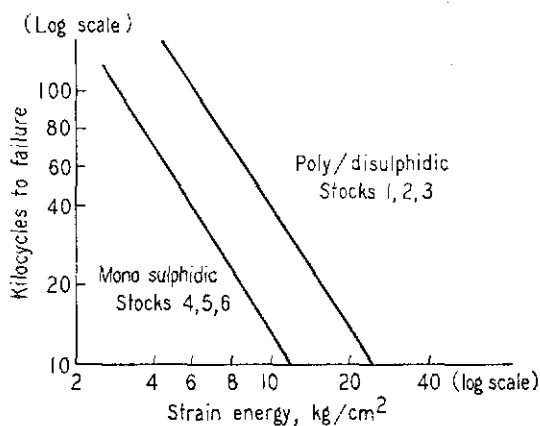

Figure 1. Comparison of fatigue lives for stocks on a strain-energy basis.
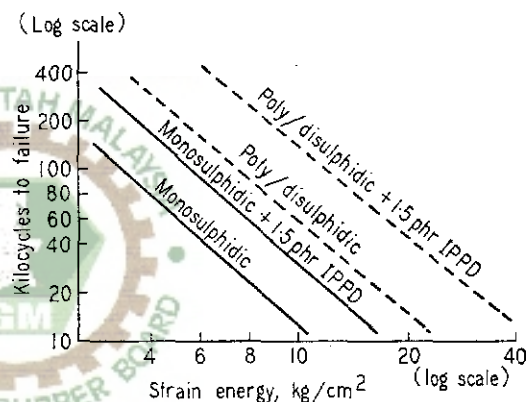

Figure 2. Effect of IPPD on stocks containing mono- and polysulphidic cross-links.

TABLE 1. FORMULATIONS USED IN STUDYING THE EFFECT OF CROSS-LINK TYPE ON FATIGUE LIFE

Masterbatch: RSS1	100
HAF black	50
Zinc oxide	5
Stearic acid	3
Process oil	3

Curing systems	Cross-link type					
	Polysulphidic			Monosulphidic		
	1	2	3	4	5	6
Sulphur, p.p.h.r.	3.0	2.75	2.5	–	0.33	–
Santocure MOR* (2 morpholino-thiobenzo-thiazole)	–	–	0.5	–	1.4	
Thiofide* [di-benzo-thiazol-2-yl disulphide] (MBTS)]	–	1.0	–	2.0	–	
Sulfasan R* (di-morpholino disulphide)	–	–	–	1.5		
Thiurad* (TMTD)	–	–	–	–	–	3.0
DPG	1.5	0.2	–	–	–	–
Optimum cure time (min) at 148°C	12	40	18	17	24	12
Type of cross-link	S_x	S_x	S_x	-S-	-S-	-S-

*A number of the trade marks referred to in this paper, including Santocure MOR, Thiofide, Sulfasan R and Thiurad, are Monsanto-registered.

Although some of the initial physical properties of these essentially monosulphidically cross-linked vulcanisates may be inferior to their polysulphidic counterparts, their retention of physical properties during high temperature oxidative ageing is vastly superior (NATURAL

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RUBBER PRODUCERS' RESEARCH ASSOCIATION, 1965a and b; SKINNER AND WATSON, 1967a and b). This also applies to retention of fatigue properties. Since the wasteful incorporation of sulphur in such main chain modifications as cyclic sulphides and pendent accelerator residues is known to promote oxidative deterioration (PARKS AND LORENZ, 1963), the more efficient usage of sulphur in cross-link formation has been advanced as the explanation of the enhanced ageing stability of these monosulphidic vulcanisates (DIBBO AND LLOYD, 1968).

'EFFICIENT VULCANISATION' SYSTEMS

Unfortunately, some of these so-called 'Efficient Vulcanisation (E.V.)' systems show certain technological disadvantages. Scorch delay periods may be so short as to be impractical, blooming may become a problem, and difficulties may be encountered in meeting modulus specifications. In an effort to overcome these disadvantages, a search was initiated for a vulcanisation system with technologically desirable scorch and cure rate characteristics, which would combine the good initial properties of conventional sulphenamide stocks with the excellent ageing performance of E.V. systems. A high initial resistance to fatigue failure combined with good retention of this property on ageing was the major target.

It was found by DIBBO AND LLOYD (1967) that combinations of N-cyclohexyl benzothiazole-2-sulphenamide (CBS) with dimorpholino disulphide (DMDS) containing a third component, tetra-methyl-thiuram di-sulphide (TMTD) as booster, enabled the cure pattern and stress–strain properties of conventional vulcanisates to be matched very closely *(Table 2)*. Although retention of these stress properties after 18 days' ageing at 90°C was considerably better than that of the conventional vulcanisate, the stock still possessed a somewhat low initial fatigue life *(Table 3)* much closer to the values characteristic of monosulphidically cross-linked vulcanisates than to those given by polysulphidic stock. This is perhaps not surprising in view of the determined structural characteristics of the vulcanisate *(Table 4)*. It must be emphasised at this

point that all correlations of fatigue with structural characteristics presented here are based on determination of the fatigue performance in black-filled stock and the analysis of structure in the corresponding gum stocks.

TABLE 2. USE OF SULPHENAMIDE/ DIMORPHOLINO DISULPHIDE/TMTD SYSTEM TO MATCH STRESS/STRAIN PROPERTIES OF CONVENTIONAL CURE SYSTEM

Base Stock: NR 100
HAF black 50
Zinc oxide 5
Stearic acid 1
Oil 3
IPPD 1

Properties	Vulcanising system				
	Conventional	Mono-/disulphidic			
			1	2	3	4
	Sulphur 2.5 CBS 0.5	CBS 1.5 DMDS 1.5 TMTD 0.0	1.4 1.4 0.2	1.3 1.3 0.4	1.0 1.0 1.0
Mooney scorch 120°C., t₅, min	24	52	35	28	16
Optimum (90%) cure 140°C., min	24	40	24	22	16
Tensile strength, kg/cm²	278	280	275	280	280
Modulus 300%, kg/cm²	130	125	125	130	135

'SEMI-EFFICIENT VULCANISATION' SYSTEM

Attention was next turned to the optimisation of accelerator blends containing only sulphenamide and dimorpholino disulphide, in the hope that by elimination of TMTD, the lowering of fatigue performance apparently caused by excessive formation of monosulphidic cross-links might be minimised. Although scorch delay in this so-called 'Semi-E.V.' system was found to be considerably higher than that of conventional sulphenamide acceleration, time to optimum cure remained essentially unchanged, and

the excellent retention of tensile strength on ageing—characteristic of E.V. systems—did not appear to be seriously compromised *(Table 5)*. Not only was the initial fatigue performance similar to that of the conventional polysulphidic sulphenamide vulcanisate, but the retention of

TABLE 3. FATIGUE LIFE OF CONVENTIONAL AND EFFICIENT VULCANISATES

Base Stock:	RSS 1	100
	HAF black	50
	Oil	5
	Zinc oxide	5
	Stearic acid	3

(a) Cross-link type

Polysulphidic		Mono- and disulphidic	
Sulphur	2.5	CBS	1.0
2-morpholinothio-		DMDS	1.0
benzothiazole	0.5	TMTD	1.0

(b) Fatigue life

	No anti-degradant	IPPD 2.0	No anti-degradant	IPPD 2.0
Kilocycles to failure at strain energy of 10 kg/cm^2	87	108	24	47

TABLE 4. COMPARISON OF CROSS-LINK STRUCTURE OF CONVENTIONAL AND EFFICIENT VULCANISATES

Base Stock:	NR (RSS1)	100
	Zinc oxide	5
	Stearic acid	1

Cross-link structure	Vulcanisate	
	Conventional	Efficient
	Sulphur 2.5 CBS 0.5	DMDS 1.0 CBS 1.0 TMTD 1.0
Initial (2Mc)$^{-1}$ × 10^5	5.84	4.13
% Monosulphidic	0	38.5
% Disulphidic	20	51.8
% Polysulphidic	80	9.7
E	10.6	3.5
E'	6.0	3.0

(2Mc)$^{-1}$ = moles of chemical cross-links per g of rubber network

E = number of sulphur atoms combined in network per chemical cross-link

E' = E after treatment with triphenylphosphine to reduce all polysulphides to monosulphides

fatigue properties after 2 days' ageing at 100°C was also considerably improved *(Table 6)*. The effect of ageing on the fatigue lives of conventional, 'E.V.' and 'Semi-E.V.' systems is depicted schematically in *Figure 3*. In view of the relatively minor differences in cross-link structure between the conventional sulphenamide stock and the 'Semi-E.V.' system, the improvement in ageing performance of the latter is probably associated with the more efficient usage of sulphur *(Table 7)* combined with avoidance of any monosulphide formation.

RESULTS AND DISCUSSION

Of the chemical processes which might contribute directly to loss of fatigue performance on ageing, two are probably of prime importance.

TABLE 5. COMPARISON OF PHYSICAL PROPERTIES OF CONVENTIONAL SULPHENAMIDE AND 'SEMI-E.V.' SYSTEM

Base Stock:	NR	100
	Process oil	8
	Zinc oxide	5
	Stearic acid	1
	GPF black	45
	Anti-oxidant	2

Properties	Vulcanising system	
	Conventional	Semi-E.V.
2-morpholinothio-benzothiazole	0.7	0.7
Sulphur	2.5	1.5
dimorpholino disulphide	0	0.5
Mooney scorch 121°C., t$_5$, min	43	61
Optimum (90%) cure 148°C., min	30	32
Tensile strength, kg/cm^2	246	242
Elongation at break, %	535	520
Modulus 300%, kg/cm^2	116	115
Tear strength, kg/cm^2	20.1	19.6
Resilience	66	69
Goodrich temperature rise, °C	24.5	24
% Retention tensile strength in oven 90°C		
6 days	90	98
9 ,,	85	95
10 ,,	68	90

TABLE 6.   FATIGUE LIFE OF CONVENTIONAL
AND SEMI-EFFICIENT VULCANISATES*

Type of vulcanisate	Vulcanising system	
	Conventional	Semi-efficient
Unaged (kc to failure)	180	180
After ageing 2 days at 100°C (kc to failure)	60	125
% Retention	33	70

*Strain energy = 10 kg/cm²

Scission processes in the main chains or in the cross-links, whether oxidatively or thermally induced, obviously play a major part. Equally important, may be cross-link shortening if this proceeds to the limit of monosulphidic cross-links. The latter process which forms part of the maturation stage of all accelerated sulphur vulcanisation reactions may be of greater significance (STUDEBAKER, 1966a and b) than has been hitherto realised in ageing processes occurring at temperatures somewhat lower than cure temperatures. It is of interest that in so far as tensile strength before ageing is concerned, the present study shows that up to 40% of monosulphidic cross-link is not detrimental. This has previously been suggested by the qualitative studies of LAL AND SCOTT

TABLE 7.   COMPARISON OF CROSS-LINK
STRUCTURE OF CONVENTIONAL AND
SEMI-EFFICIENT VULCANISATES

Cross-link structure	Vulcanisate	
	Conventional	Semi-efficient
	Sulphur 2.5 CBS 0.5	Sulphur 1.5 CBS 0.5 DMDS 0.5
Initial $(2Mc)^{-1} \times 10^5$	5.84	5.62
% Monosulphidic	0	0
% Disulphidic	20	26
% Polysulphidic	80	74
E	10.6	7.1
E'	6.0	3.0

(1966) on the effect of extended triphenylphosphine treatment on the tensile strength of natural rubber gum stocks vulcanised with sulphur/DPG. Such proportions of monosulphidic cross-links, whether present initially, or formed during ageing, will apparently lower resistance to fatigue failure. If extrapolation of the structural characteristics of gum stock to the analogous black-filled stock is permissible, then the loss of fatigue resistance observed in conventional sulphenamide stock during two days at 100°C is not in any way due to such monosulphide formation. No monosulphide could be detected in PPD containing sulphenamide accelerated gum stock after two days at 100°C,
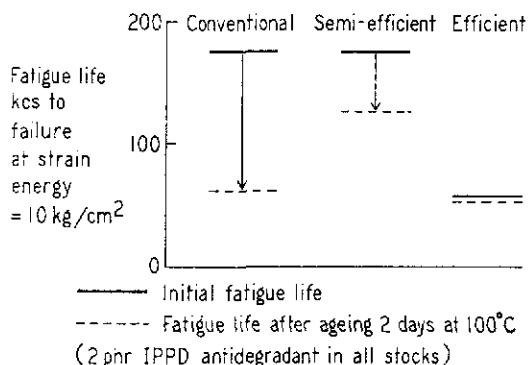

Figure 3.   Effect of ageing on the fatigue properties.

but this observation does not, of course, preclude its formation in different stock under similar ageing conditions.

In considering the maturing of initially formed networks, N.R.P.R.A. workers (BATEMAN et al., 1963b) cite 'efficient' MBT-accelerated cure systems at 100°C and zinc dimethyldithiocarbamate-accelerated sulphur vulcanisation at 100°C as being typical of systems which show a relatively rapid, efficient crosslink shortening and a slow, complex-shortening respectively. In the former, extended cure times lead to vulcanisates of progressively higher modulus, whereas in the latter crosslink decomposition leading to modulus reversion becomes important. One would expect such thermally induced reactions to be super-

imposed on the normal oxidative reactions, when air ageing of these vulcanisates is carried out at 100°C. One might deduce that, on ageing, the 'efficient' MBT system would combine a low level of oxidative chain scission with some tendency towards an increase in cross-link density accompanied by monosulphide formation. The zinc dimethyldithiocarbamate-accelerated system on the other hand, with much main-chain modification, might be expected to give relatively little monosulphide, but would be extremely prone to undergo oxidative chain scission accompanied by non-oxidative and perhaps oxidative scission of cross-links. In general, therefore, the MBT stock would be expected to show good ageing characteristics, and the dithiocarbamate stock poor ageing.

Since structural characterisation of these natural rubber gum stocks has already been carried out (BATEMAN *et al.*, 1963b) it was decided to compare the conventional physical properties and resistance to fatigue failure both before and after ageing of analogous black reinforced stocks. Results are presented in *Table 8* alongside conventional sulphenamide and 'Semi-E.V.' stocks for comparison, and the reported N.R.P.R.A. analyses results for the gum stocks are reproduced in *Tables 9* and *10*.

The detailed results set out in *Table 8* show that the 'efficiently' cured MBT black stock does indeed show good retention of physical properties on ageing, with a very slight superiority over the semi-efficient system. Both are significantly better than the conventional sulphenamide system, which in turn is considerably better than the fast ageing dithiocarbamate stock. In so far as retention of flex life is concerned *(Table 11)*, the position is slightly altered. The superiority of the dimorpholino disulphide containing 'Semi-E.V.' system over the 'efficient' MBT system is quite marked, and the conventional sulphenamide and dithio-

TABLE 8. PHYSICAL PROPERTIES AND RESISTANCE TO FATIGUE FAILURE BEFORE AND AFTER AGEING OF EFFICIENT MBT AND ZINC DIMETHYLDITHIOCARBAMATE-ACCELERATED STOCK

Base stock:	NR	100
	Process oil	8
	Zinc oxide	2
	GPF black	45
	N-phenyl-N'-1,3-dimethyl butyl PPD	2

Item	Conventional sulphenamide	Semi-E.V.	Efficient MBT	ZnDMC
Lauric acid	1.0	1.0	10.0	——
Sulphur	2.5	1.5	1.5	2.0
2-morpholinothiobenzothiazole	0.7	0.7	—	—
Additional zinc oxide	3.0	3.0	3.0	—
Dimorpholino disulphide	—	0.5	—	—
MBT	—	—	1.5	—
Zinc dimethyldithiocarbamate	—	—	—	2.0
Cure temperature	148°C	148°C	100°C	100°C
Cure time	17 min	16 min	24 h	2 h
Before ageing:				
Tensile strength, kg/cm²	280	282	228	297
Elongation at break, %	530	550	400	600
Modulus 300%, kg/cm²	121	111	162	104
After 2 days at 100°C:				
Tensile strength, kg/cm²	199	223	186	152
Elongation at break, %	410	460	340	220
Modulus 300%, kg/cm²	143	130	163	—
% Retention tensile strength	71	79	82	51
% Retention elongation at break	77	84	85	37

TABLE 9. STRUCTURE OF EFFICIENT MBT-ACCELERATED VULCANISATE

Cure time(h) at 100°C	$10^5/2Mc$	E	E′	Cross-link structure	
				Mono-sulphide %	Poly-sulphide %
3	1.4	6.2	2.4	0	100
24	8.5	3.1	2.2	—	—
144	13.0	2.4	2.0	55	45

[From 'Proceedings of the N.R.P.R.A. Jubilee Conference, Cambridge, 1964', *Table 4*, 183, (London: Maclaren and Sons Ltd.)]

TABLE 10. STRUCTURE OF ZINC DIMETHYLDITHIOCARBAMATE-ACCELERATED VULCANISATE

Cure time (h) at 100°C	$10^5/2Mc$	E	E′	Cross-link structure
0.25	1.50	7.0	1.3	No monosulphide at 2 hours, and very little at 20 hours
2.0	4.03	12.5	6.3	
20.0	3.12	18.0	13.7	

[From 'The Chemistry and Physics of Rubber-like Substances', Chapter 15, *Tables 15.9* and *15.10*, (London: Maclaren and Sons Ltd).]

carbamate accelerated system show a much lower and almost equal percentage retention of flex life. To some extent, the low initial fatigue life of the 'efficient' MBT system may reflect an undesirably high content of monosulphidic cross-links in the starting material, but if this were so, a better ageing performance might have been expected.

CONCLUSIONS

A distinct advance in improved ageing with much improved retention of fatigue properties

TABLE 11. COMPARISON OF RESISTANCE TO FATIGUE FAILURE OF CONVENTIONAL, SEMI-E.V., EFFICIENT MBT AND ZnDMC SYSTEMS*

Resistance to fatigue failure	Conventional	Semi-EV	Efficient MBT	ZnDMC
Kilocycles to failure before ageing	89	76	34	52
Kilocycles to failure after 2 days at 100°C	31	53	19	19
% Retention	35	70	56	37

* Strain energy = 10 kg/cm²

is shown. At this stage, a significant correlation between the extent of usage of sulphur in main-chain modifications, and the rapidity of loss of flex properties during ageing is still apparent. The present results do not, however, provide any further explanation for this correlation. It is tempting but premature to speculate that these main-chain modifications lead to an enhancement of oxidative chain scission processes. Not only does the dithiocarbamate-based vulcanisate with the most rapid ageing characteristics show the greatest tendency towards modulus reversion, but the three stocks with the best retention of fatigue properties are known to show minimal reversion behaviour. Maturation reactions obviously cannot be ignored, and the full explanation must await further more detailed study. Comparison with conventional and E.V. systems over a range of ageing would be of considerable value.

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DISCUSSION

Chairman: Dr. W. F. Watson

Dr. P. Thirion asked if the relationships between fatigue life and strain energy in peroxide and sulphur vulcanisates had been compared. Dr. McCall said he had not examined peroxide vuncalisates, which were reported in the literature to have similar fatigue life to monosulphide vulcanisates. Dr. J.I. Cunneen said that semi-E.V. compounds were most interesting because they had better fatigue properties after ageing than conventional vulcanisates. Dr. McCall had attributed these to less sulphur combined as main chain modifications (lower E and E'values) in the semi-E.V. compounds giving better ageing properties. However, Dr. Cunneen could not reconcile this with his previous demonstration (CUNNEEN, 1962) that the polysulphide content determined mainly the oxidation characteristics of protected vulcanisates and that other sulphur — such as main chain modifications — played a minor role. Present knowledge was inadequate to explain differences in ageing between semi-E.V. and conventional compounds. Dr. McCall said that the rate of oxidation had been measured in semi-E.V. systems and it was perhaps not critical, but entropy factors might be influencing the structures formed during oxidation and thus affecting properties like tensile strength.

Mr. E.A. Murphy asked if the results obtained with different sulphur cross-linking systems applied also to synthetic polyisoprene. Dr. McCall said he had not investigated the point, but he expected to see no difference. Dr. J.D. D'Ianni also reported no obvious differences. Dr. G.M. Bristow confirmed that no differences in fatigue resistance at 21°C had been found in vulcanisates from natural rubber and high *cis*-1,4-polyisoprene.