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Contents

Preliminary Observations on the Induction of Precocious Flowering in Hevea Brasiliensis by PP333

H.Y. YEANG* AND Z. SAMSUDDIN*

The growth retardant PP333, applied as a soil drench, induced precocious flowering in young ungirdled Hevea *planted in polybags or in the field. Viable pollen and seeds were obtained from the treated plants. Some effects of PP333 on floral and vegetative morphology are described.*

Hevea is a perennial crop that has a juvenile phase of four to five years during which the trees do not flower. This vegetative phase imposes a limitation to the extent by which the breeding cycle can be shortened. Precocious flowering in *Hevea* would enable a reduction in the duration between generations which would in turn enable an acceleration of the advancement in breeding and selection of the crop. Various benefits relating to hand-pollination practice may also be derived from early flowering in young rubber plants. Among these are the convenience of hand-pollination from the ground, more effective pathogen control leading to better fruit-set[1-3] and an extended duration of flowering which may help to overcome non-synchrony in flowering between clones[1,2].

Girdling of the trunk or branches (ring barking) has generally been found to be the most effective means of inducing early flowering in *Hevea*[1,2,4-7]. Chemical treatments have occasionally been reported to be effective, but often, their effectiveness have been evident only when complemented by girdling[1,2,6,7].

Flowering has been reported to be enhanced in the apple tree after treatment with the growth retardant PP333 (paclobutrazol)[8]. This paper describes preliminary findings on the effect of PP333 on the induction of precocious flowering in young ungirdled *Hevea* plants.

MATERIALS AND METHODS

Experiment 1a. Eighteen-month-old RRIM 600 plants grown in 36×62 cm polybags were untreated (control), repeatedly girdled or received a single dose in varying strengths of (2RS 3RS)-1-(-4-chlorophenyl)-4,4-dimethyl-2-(1H-1,2,4-triazol-1-yl) penton-3-ol, also known as paclobutrazol or PP333 (Imperial Chemical Industries, Plant Protection Division, UK). Ten plants were allotted to each treatment.

Experiment 1b. Eighteen-month-old PB 5/51 plants in 36×62 cm polybags were treated as in *Experiment 1a,* but the PP333-treated plants received a second application six weeks after the first dose. Ten plants were allotted to each treatment.

Experiment 2a. In the field, treatments were assigned to fourteen-month-old RRIM 600 plants in three randomised blocks of sixteen trees per treatment. The plants were untreated (control) or given a single dose of PP333 of varying strengths.

Experiment 2b. Fourteen-month-old GT 1 plants were laid out in two blocks of twelve plants per treatment in the field. Treatments similar to those in *Experiment 2a* were applied but the PP333-treated plants received an additional second dose three months after the initial application. A repeated girdling treatment was also included.

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*Rubber Research Institute of Malaysia, P.O. Box 10150, 50908 Kuala Lumpur, Malaysia

In the above experiments, repeated girdling was carried out by removing a 2 mm ring of bark from the stem at approximately monthly intervals. Application of PP333 was by soil drench and quantities of PP333 cited in the text refer to the active ingredient (a.i.). The compound was made up to volume with water and 100 ml were applied per polybag plant and 1 litre per field plant.

Recordings on flowering were made once a month and scores of flowering plants and flowering intensity (number of flower panicles per flowering tree) pertained to the day of observation. As such, they do not denote the total number of flowering trees or flower panicles present during the entire month but reflect the relative intensities of flowering between the different treatments on the day of observation.

To germinate pollen, staminal columns were collected in a glass vial and allowed to dehisce in the laboratory. The pollen grains were suspended in a hanging drop of 0.01% boric acid containing 15% sucrose. Pollen germination was scored the following morning under a microscope.

RESULTS

Flowering in Polybag Plants

Experiment 1a. Flowering was first observed in RRIM 600 polybag plants five months after they were treated with PP333 at a rate of 0.75 g per plant. By the eleventh month after treatment, five out of ten treated plants had flowered *(Table 1)*. A lower rate of application of 0.5 g was also effective but the effectiveness diminished when only 0.25 g was applied. Repeated girdling induced flowering in only one out of ten plants and a high incidence of dieback was observed. Flowering was not observed in any of the untreated control plants.

Experiment 1b. With PB 5/51 polybag plants, flowering was first observed four months after their first treatment. No difference was observed between the three rates of application used (2×0.75 g, 2×0.5 g, 2×0.25 g per plant). In each instance, three plants out of ten were induced to flower. As with RRIM 600, plants subjected to repeated girdling were prone to dieback. Flowering was observed in two plants while none of the untreated control plants flowered.

TABLE 1. CUMULATIVE INCIDENCE[a] OF FLOWERING IN POLYBAG PLANTS THAT WERE REPEATEDLY GIRDLED OR TREATED WITH PP333

Treatment	Incidence of flowering	
	RRIM 600 (Experiment 1a)	PB 5/51 (Experiment 1b)
Control	0	0
Repeated girdling	1	2
PP333[b]		
0.25 g	2	
0.50 g	4	
0.75 g	5	
2×0.25 g		3
2×0.50 g		3
2×0.75 g		3

[a]Number of flowering plants out of ten plants per clone
Observations were made 11 months after commencement of the treatments.

[b]RRIM 600 plants received a single application of PP333 while PB 5/51 plants received a second application after six weeks.

In both *Experiments 1a* and *1b,* plants that were treated with PP333 appeared to be in a state of stress. Leaf abscission was observed a few weeks after treatment while retarded growth was sustained over a year of observation. The new growth occurring after treatment in some of the treated plants had short internodes while leaf petioles were similarly short and closely inserted within the flush. There was however no clear relationship between this growth habit and the incidence of flowering. Flowering was also induced in plants not markedly exhibiting the trait. As in the case of the foliage, the PP333-induced inflorescences appeared similarly clumped and compact with the flowers packed very close together *(Figure 1)*. Premature flower drop was frequently observed.
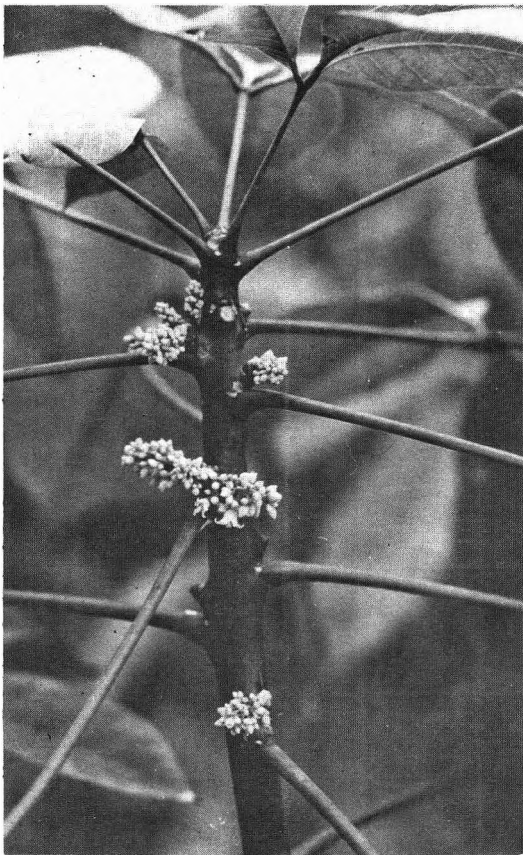
Figure 1. Compact panicles on a two-year-old PB 5/51 polybag plant treated with PP333.

Flowering in Field Planting

Experiment 2a. Following PP333 treatment of the plants in the field in July, flowering in RRIM 600 was first observed six months later, coinciding with the main flowering season that followed wintering. The chemical enhanced wintering (which is normally mild or absent in plants of this age). The most effective among the dosages tested was 10 g and this induced flowering in twenty-six out of forty-eight plants (54%) in the duration of a year from the time of first flowering *(Figure 2)*. Lower rates of 0.5 g to 5 g were relatively less effective. A small number of untreated trees flowered towards the later part of the study *(Figure 2)*. In terms of the intensity of flowering (number of flower panicles per flowering tree), an optimum dosage was not readily discernible from the limited observations *(Table 2)* but flowering plants treated with 2 g and 10 g PP333 bore the largest number of inflorescences.

Inflorescences of PP333-treated plants appeared normal in their development with no obvious signs of growth inhibition *(Figure 3)*.

Experiment 2b. Compared with RRIM 600, GT 1 plants treated with PP333 in the field showed markedly more severe wintering with branches completely bare in many instances. Inflorescences subsequently developed on the almost bare branches of this clone. They consisted of compact panicles with closely packed flowers borne on very short pedicels *(Figure 4)*. Flowering tended to be relatively sparse in PP333-treated plants that had copious refoliation.

Flower-induction in GT 1 was most effective with 2×5 g PP333, flowering being first observed six months from the initial treatment. Within a year from the first observation of flowering, seventeen out of twenty-four plants (71%) had flowered *(Figure 5)*. Repeated trunk girdling was almost as effective, while rates higher or lower than 2×5 g were less effective. Only one untreated tree flowered during the period of observation *(Figure 5)*. With GT 1, plants treated with 2×2 g and 2×5 g PP333 had the largest number of panicles per flowering plant *(Table 2)*. On refoliation,
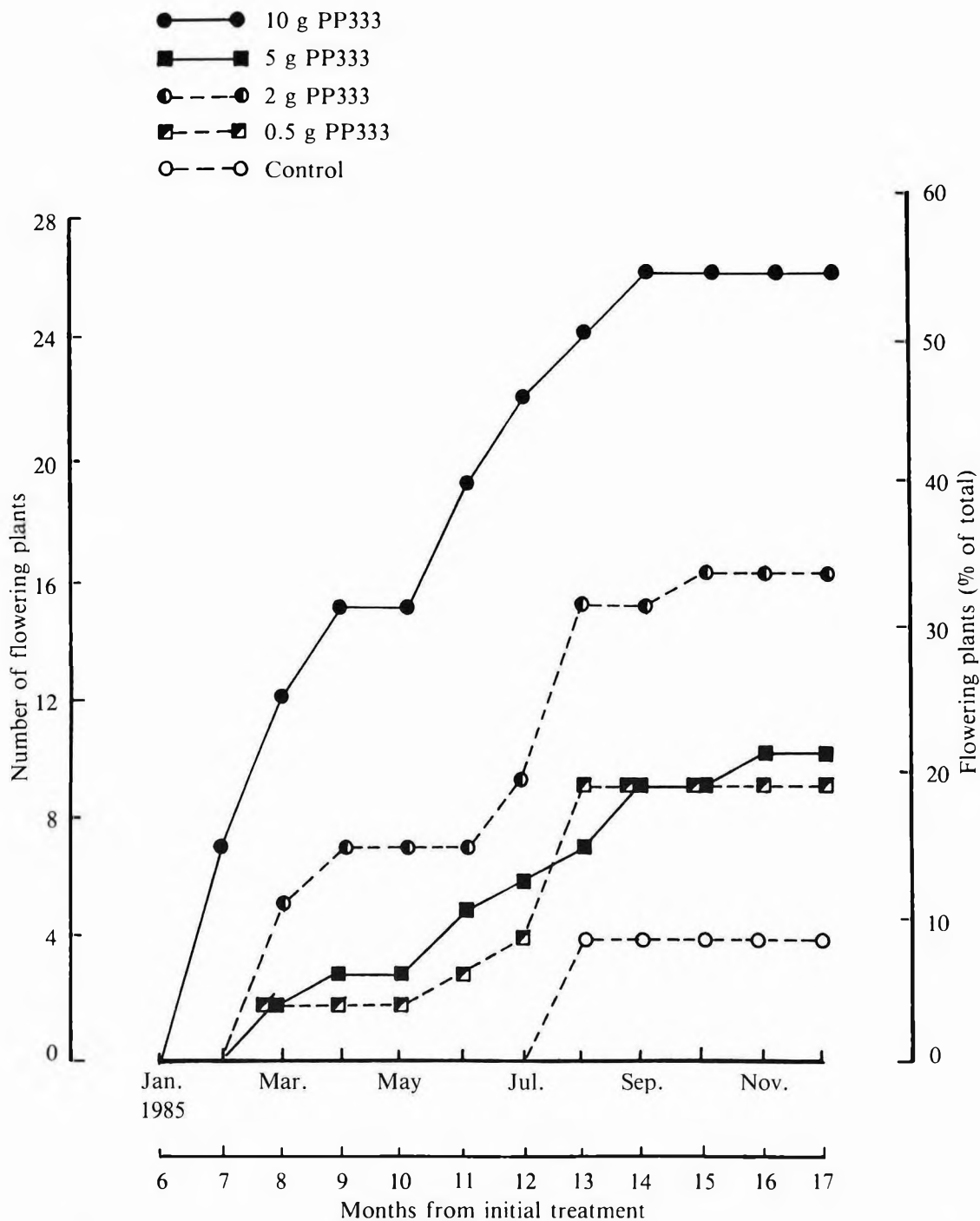
Figure 2. Cumulative incidence of flowering in RRIM 600 plants in the field. Fourteen-month-old plants (forty-eight per treatment) were given a single application of PP333 in July 1984.

TABLE 2. INTENSITY OF FLOWERING[a] IN THREE-YEAR-OLD PLANTS THAT
WERE REPEATEDLY GIRDLED[b] OR TREATED WITH PP333

| Treatment | Intensity of flowering | |
	RRIM 600 (Experiment 2a)	GT 1 (Experiment 2b)
Control	4.3	1
Repeated girdling	—	7.8
PP333[c]		
0.5 g	6.4	
2 g	15.1	
5 g	5.1	
10 g	9.2	
2 × 0.5 g		2.7
2 × 2 g		21.0
2 × 5 g		19.2
2 × 10 g		8.2

[a]Number of flowering panicles per flowering plant; mean of one observation each in July, August and September 1985

[b]GT 1 only

[c]RRIM 600 plants received a single application of PP333 while GT 1 plants received a second application after three months.
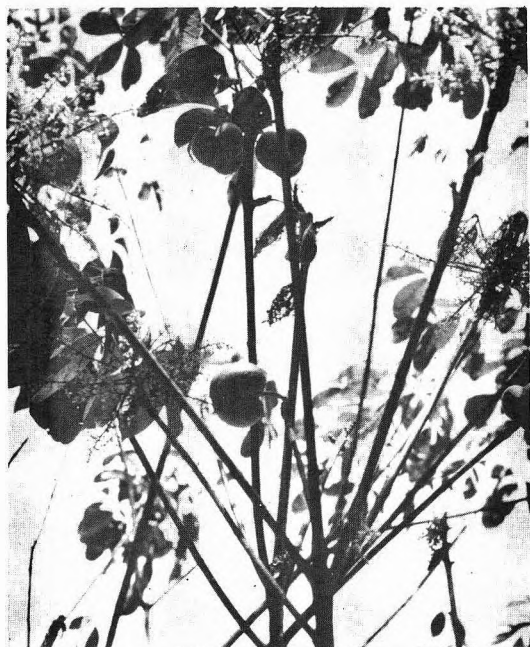
Figure 3. Flowers and fruits on a two-year-old RRIM 600 plant in the field treated with PP333.

Figure 4. Compact panicles on a two-year-old GT 1 plant in the field treated with PP333.
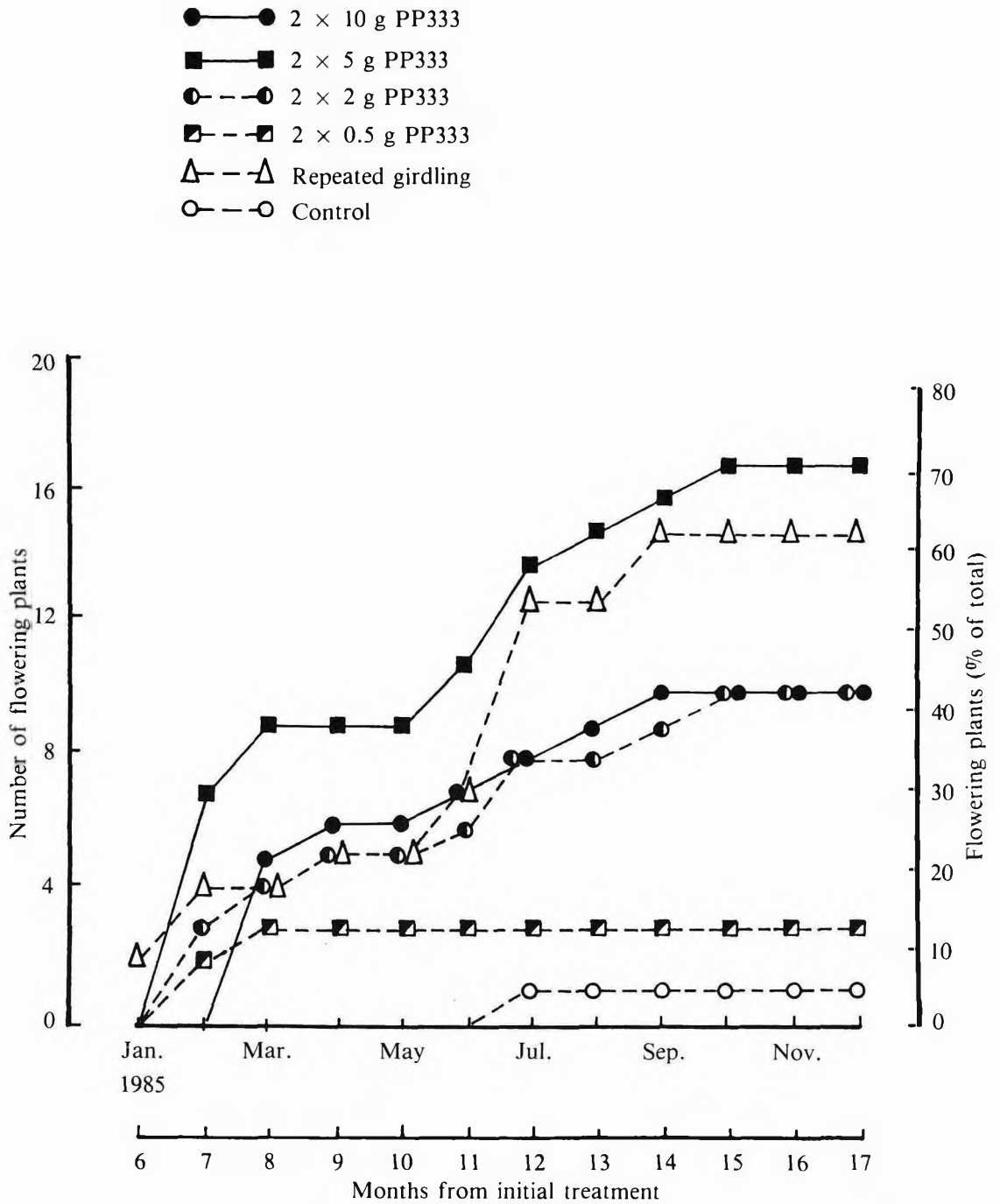
Figure 5. Cumulative incidence of flowering in GT 1 plants in the field. Fourteen-month-old plants (twenty-four per treatment) were treated with PP333 in July and October 1984. The repeated girdling treatment commenced from July 1984.

growth retarding effects on the foliage similar to those seen in polybag plants were observed. Lateral shoots failed to extend and closely packed clumps of leaves with short petioles were held very close to the main stems *(Figure 6)*.

Figure 6. Growth habit of foliage in a two-year-old GT 1 plant in the field treated with PP333 showing the clumping effect on the leaves.

As in flowering induced by girdling[2], flowering induced by PP333 in both the field experiments appeared to be synchronised to the seasonal cycle of mature trees. Flowering was most evident during the two annual flowering seasons in February/March and July/August *(Figure 7)*. Flowers were also observed at other times of the year, but in smaller numbers.

Pollen and Seed Germination

Over 6000 pollen grains from RRIM 600 flowers induced by PP333 were scored for germination and matched with a similar number of pollen grains from untreated mature trees of the same clone which served as controls. Pollen germination was generally poor, possibly due to the uncharacteristically wet weather. The rate of germination ranged from 0% to 33% for control pollen and 0% to 84% for pollen derived from induced flowers. The mean germination rates were 8% and 15% respectively.

Hand-pollination using the PP333-induced flowers was not attempted but fruit-set from free pollination was readily observed, particularly in the RRIM 600 plants *(Figure 3)*. Out of seventy-two seeds harvested from RRIM 600 plants treated with PP333, thirty-two germinated giving a germination rate of 44.4%.

DISCUSSION

The results of this preliminary study show that PP333 induces precocious flowering in ungirdled young rubber plants. The chemical compound was effective both with polybag plants (which do not respond well to girdling) and plants in the field. In the latter, an application of 10 g a.i. — applied as a single dose (in RRIM 600) or two split doses of 5 g (in GT 1) — was most effective in bringing young rubber plants into flowering. Susceptibility to the growth retarding effect of PP333 in vegetative and floral development differed between the clones used in the study, but there was insufficient evidence to indicate if this was a clonal characteristic. The severity of retardation exhibited did not, however, necessarily reflect the effectiveness in the induction of flowering. The seasonality of response to floral induction suggested an interaction between stimulus by PP333 and climatic factors. Other factors (soil types, rootstocks, shade, *etc.*) might also have affected PP333 response and this could have given rise to the situation in RRIM 600 *(Figure 2)* where consistent correspondence between flowering responses and the chemical dosages applied was lacking.
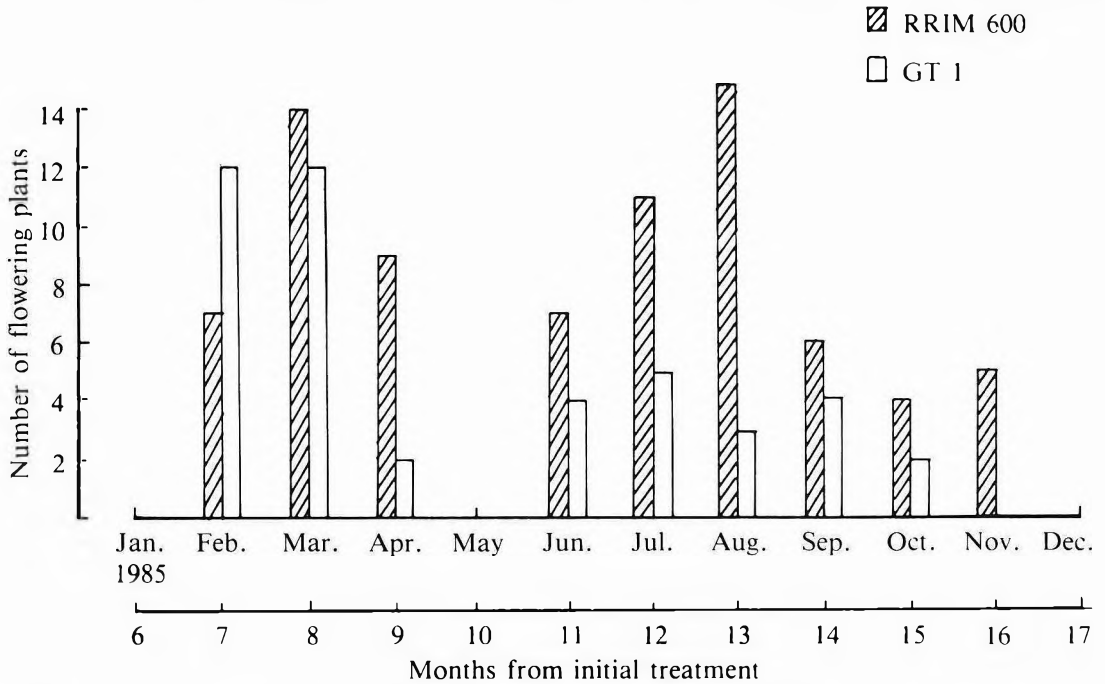
Figure 7. Seasonal variation in precocious flowering induced by PP333. Results combined from all dosages of PP333 applied and are based on a single observation per month.

Pollen germination was generally poor in samples from PP333-treated plants, but this could have been a pathological problem linked to the very wet weather experienced. In fact, pollen from control mature trees fared even worse although no significance should be attached to this observation in view of the overall low germination rate. There was hence no evidence from the available data of adverse effect on pollen germination arising from PP333 treatment.

Seed germination was moderately low in harvests from PP333-treated plants. Nevertheless, the figure of 44% is comparable to some of the germination rates in seeds obtained from girdled trees in previous studies[1,2].

The results from this preliminary study show that PP333 may be kept in view as a potential alternative to stem or branch girdling as a means of inducing precocious flowering to aid *Hevea* breeding. The effectiveness of PP333 in flower induction, the simplicity of its application and its ability to retard growth (thereby keeping the plant short and amenable to pathogen control and hand-pollination from the ground) are points in its favour. However, further evaluation of the chemical needs to be carried out before firm conclusions can be drawn.

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Weekly Tapping of Rubber Trees: Agronomical, Physiological and Economic Aspects

J.M. ESCHBACH*

The change from full-spiral twice a week to half-spiral stimulated aims to decrease tapping intensity and increase productivity of the tapper. The best way of doing this is to decrease the tapping frequency and increase stimulation to maintain satisfactory yield per tree.

This paper summarises the results obtained with weekly tapping frequency of d/6 6d/7 compared with a twice-weekly frequency of d/3 6d/7 on several clones in the Ivory Coast.

In spite of increased stimulation, yields obtained were very often inferior, i.e. about 10% less than those obtained with two tappings per week. Not all clones react in the same way to a decrease in tapping intensity.

Secondary characteristics such as dry rubber content, sucrose content and incidence of dry trees were better than with half-weekly tapping in spite of the number of stimulations being twice as high.

From an economic view-point, weekly tapping greatly reduces the need for labour. The break-even point which depends on the market price and the cost of labour, if not already reached in the Ivory Coast on existing estates, has every chance of being so in view of the socio-economic advances in the developing countries.

Hevea latex collection is labour-consuming; shortage of and high-priced labour dictate the need for research efforts on labour-saving exploitation systems capable of maintaining a good level of production per hectare[1,2,3]. Stimulation, recommended for thirty years is the usual exploitation method[4] in the Ivory Coast and it allowed tapping intensity to be considerably decreased by replacing full-spirals (S) with half-spirals (½S) while maintaining a good level of production especially since ethephon was used[5,6].

However, it is the reduction in tapping frequency that allowed labour requirements to be decreased. During the last decade, a weekly tapping system with ½S (d/6 6d/7) has been compared with a twice-weekly tapping control system with ½S (d/3 6d/7). Preliminary results have already been published[7]; this paper reviews the results obtained on various clones and sites for several years.

MATERIAL AND METHODS

The experiments classified according to the clone and the year the experiments commenced are shown in *Table 1*. Seven clones were examined on a total of three sites. The experiments started in 1976, on trees at opening or already exploited trees, according to a split or one-tree plot block statistical design. The international notation of tapping systems is shown in *Appendix A*.

Details of the experimental treatments are shown in *Tables 2–5*. For trees at opening, 5% ethephon was applied. The supporting substance of ethephon was palm oil and various application methods were used: 1 cm on the panel for trees at opening and 2 cm on scraped bark for older trees.

For *Experiments 1C, 1D* and *2C,* latex and coagulated latex (cuplump) production for each

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TABLE 1. DETAILS OF EXPERIMENTS

Clone	Experiment	Commencement	Design (trees per treatment)	
GT 1	1 A	7th year of tapping	Block	(300)
	1 B	5th year of tapping	Block	(360)
	1 C	At opening	Block	(400)
	1 D	At opening	Block	(560)
PR 107	2 A	7th year of tapping	Block	(320)
	2 B	7th year of tapping	Block	(300)
	2 C	12th year of tapping	Block	(1680)
PB 235	3 A	At opening	Split-plot	(320)
	3 B	At opening	One-tree	(33)
	3 C	At opening	Block	(460)
PB 217	4 A	At opening	One-tree	(33)
	4 B	At opening	Block	(400)
PR 261	5 A	At opening	One-tree	(33)
	5 B	At opening	Block	(400)
AVROS 2037	6	At opening	Block	(360)
PB 5/51	7	3rd year of tapping	Block	(320)

plot was measured and at every tapping, dry rubber content (d.r.c.) was determined. For *Experiments 3C, 4B* and *5B,* cuplump production was measured on a weekly basis. The d.r.c. of cuplump was estimated at 50%. For the other experiments, latex production from several tappings was measured every four weeks. The d.r.c. of the coagula of each treatment was measured at each control to determine dry rubber weight.

Latex analyses to measure d.r.c. and sucrose content were carried out on all the latex collected in one tapping.

The number of trees producing no more latex (dry trees) was counted each year and the percentage of diseased cut length was expressed according to the total cut length, for each treatment (dryness, percentage cut length).

RESULTS

Clone GT 1

The results obtained for GT 1 are shown in *Table 2* and *Figure 1.* For trees at opening *(Experiments 1C* and *1D)* on *Panels BO-1* and *BO-2,* latex production obtained with one weekly tapping (d/7) was always lower than that obtained with twice-weekly tappings (d/3 6d/7), although the number of stimulations was two to three times higher. Response to stimulation was slightly better on scraped bark and with ten stimulations; the cumulative production obtained was 82% of that of the control. With twelve stimulations on the panel, 85% of the production of the control was obtained.

For older trees *(Experiments 1A* and *1B)* on Panels *BI-1* and *BI-2,* relative productions were

TABLE 2. COMPARISON OF WEEKLY AND TWICE-WEEKLY TAPPINGS ON GT 1

Experiment (duration)	Treatment		Production			Dry extract (%)	Sucrose (mm serum)	Dryness	
			Total (g/tree)	Mean (g/tree/year)	Control (%)			Dry trees (%)	Cut length (%)
1 A (9 years)	½S d/3 6d/7 ET 5% Ba 2 (2)	4/y	58 585	6 695	100	39.4	24.6	0.5	2.2
	½S d/6 6d/7 ET 5% Ba Pa 2 (1+1)	8/y	52 270	5 974	89	43.1[a]	42.2[a]	1.3	4.6
	½S d/6 6d/7 ET 5% Ba Pa 2 (1+1)	10/y	56 278	6 432	96	40.9[a]	42.1[a]	0.4	2.6
1 B (8 years)	½S d/3 6d/7 ET 5% Ba 2 (2)	4/y	45 735	5 901	100	37.3	11.2	14.0	51.0
	½S d/6 6d/7 ET 5% Ba Pa 2 (1+1)	8/y	41 985	5 417	92	41.3[a]	20.7[a]	10.0	35.0[a]
	½S d/6 6d/7 ET 5% Ba Pa 2 (1+1)	10/y	43 320	5 590	95	35.7	20.6[a]	13.0	33.0[a]
1 C (3 years)	½S d/3 6d/7 ET 5% Ba 2 (2)	4/y	20 152	4 478	100	—	—	7.8	—
	½S d/6 6d/7 ET 5% Pa 1 (1)	8/y	17 151	3 811	85	—	—	5.1	—
1 D (4 years)	½S d/6 6d/7 ET 5% Pa 1 (1)	6/y	16 124	4 031	100	32.2	—	3.6	—
	½S d/6 6d/7 ET 5% Ba 1 (1)	6/y	12 951[a]	3 238[a]	81	34.7[a]	—	0.6	—
	½S d/6 6d/7 ET 5% Ba 1 (1)	8/y	12 800[a]	3 200[a]	80	34.4[a]	—	1.8	—
	½S d/6 6d/7 ET 5% Ba 1 (1)	10/y	13 284[a]	3 321[a]	82	34.0[a]	—	0.4	—
	½S d/6 6d/7 ET 5% Pa 1 (1)	8/y	12 593[a]	3 148[a]	78	35.1[a]	—	1.6	—
	½S d/6 6d/7 ET 5% Pa 1 (1)	10/y	12 422[a]	3 106[a]	77	33.6[a]	—	2.8	—
	½S d/6 6d/7 ET 5% Pa 1 (1)	12/y	13 742[a]	3 436[a]	85	32.5	—	1.5	—

[a]Significantly different from the control at the 0.05 level

TABLE 3. COMPARISON OF WEEKLY AND TWICE-WEEKLY TAPPINGS ON PR 107

Experiment (duration)	Treatment		Production			Dry extract (%)	Sucrose (mm serum)	Dryness	
			Total (g/tree)	Mean (g/tree/year)	Control (%)			Dry trees (%)	Cut length (%)
2 A (9 years)	½S d/3 6d/7 ET 5% Ba 2 (2)	4/y	52 354	5 983	100	34.0	32.8	0.6	4.2
	½S d/6 6d/7 ET 5% Ba Pa 2 (1+1)	8/y	43 833[a]	5 009[a]	84	40.9[a]	32.5	2.1	6.9
	½S d/6 6d/7 ET 5% Ba Pa 2 (1+1)	10/y	48 652	5 560	93	42.0[a]	29.7	0.7	3.7
2 B (2 years)	½S d/3 6d/7 ET 5% Ba 2 (2)	4/y	11 646	5 823	100	34.9	9.6	1.0	9.6
	½S d/6 6d/7 ET 5% Ba Pa 2 (1+1)	10/y	10 445	5 223	90	38.8	8.0	2.3	7.4
2 C (5 years)	½S d/3 6d/7 ET 2.5% Ba 2 (2)	4/y	32 946	6 589	100	38.6	—	10.7	—
	½S d/6 6d/7 ET 4% Ba 1 (1)	10/y	29 535	5 907	90	39.2	—	8.6	—
	½S d/6 6d/7 ET 8% Ba 1 (1)	10/y	31 185	6 237	95	37.2	—	6.9	—
	½S d/6 6d/7 ET 8% Ba 1 (1)	10/y	31 822	6 364	97	37.5	—	8.1	—

[a]Significantly different from the control at the 0.05 level

TABLE 4. COMPARISON OF WEEKLY AND TWICE-WEEKLY TAPPINGS ON PB 235

Experiment (duration)	Treatment	Production			Dry extract (%)	Sucrose (mm serum)	Dryness	
		Total (g/tree)	Mean (g/tree/year)	Control (%)			Dry trees (%)	Cut length (%)
3 A (4 years)	½S d/3 6d/7 ET 2.5% Ba 2 (2) 2/y	14 513	3 628	100	33.1	5.5	4.1	20.1
	½S d/6 6d/7 ET 2.5% Pa 1 (1) 4/y	10 795[a]	2 699[a]	74	43.4[a]	9.1[a]	0.0	4.1[a]
	½S d/6 6d/7 ET 2.5% Pa 1 (1) 8/y	11 171[a]	2 793[a]	77	40.7[a]	11.1[a]	0.3	6.8[a]
	½S d/6 6d/7 ET 2.5% Pa 1 (1) 12/y	11 878[a]	2 970[a]	82	39.2[a]	6.3[a]	0.8	8.1[a]
3 B (2 years)	½S d/3 6d/7 Not stimulated	6 289	3 145	100	36.9	10.4	—	3.3
	½S d/6 6d/7 ET 2.5% Pa 1 (1) 4/y	6 216	3 108	99	42.7[a]	7.4[a]	—	10.3
	½S d/6 6d/7 ET 2.5% Ba 2 (2) 2/y	6 632	3 316	100	—	—	9.4	27.7
	½S d/6 6d/7 ET 2.5% Pa (1) 4/y	5 488[a]	2 744[a]	83	—	—	5.2	14.8

[a]Significantly different from the control at the 0.05 level

TABLE 5. COMPARISON OF WEEKLY AND TWICE-WEEKLY TAPPINGS ON SEVERAL CLONES

Clone	Experiment (duration)	Treatment		Production		Control (%)	Dry extract (%)	Sucrose (mm serum)	Dryness	
				Total (g/tree)	Mean (g/tree/year)				Dry trees (%)	Cut length (%)
PB 217	4 A	½S d/3 6d/7 ET 2.5% Ba 2 (2)	4/y	6 238	3 119	100	31.2	28.4	—	0.6
	(2 years)	½S d/6 6d/7 ET 2.5% Pa 1 (1)	8/y	4 489^a	2 427^a	72	39.7^a	19.7^a	—	1.3
		½S d/6 6d/7 ET 2.5% Pa 1 (1)	12/y	4 853^a	2 427^a	78	37.7^a	22.4^a	—	3.3
	4 B	½S d/3 6d/7 ET 2.5% Ba 2 (2)	2/y	2 752	2 752	100	—	—	0.7	—
	(1 year)	½S d/6 6d/7 ET 2.5% Pa 1 (1)	6/y	2 113^a	2 113^a	77	—	—	0.2	—
PR 261	5 A	½S d/3 6d/7 ET 2.5% Ba 2 (2)	4/y	6 600	2 200	100	35.0	28.0	—	0.8
	(3 years)	½S d/6 6d/7 ET 2.5% Pa 1 (1)	8/y	4 147^a	1 382^a	63	42.7^a	30.0	—	0.0
		½S d/6 6d/7 ET 2.5% Pa 1 (1)	12/y	4 923^a	1 641^a	75	41.2^a	27.2	—	2.1
	5 B	½S d/3 6d/7 ET 2.5% Ba 2 (2)	3/y	3 179	1 907	100	—	—	1.4	—
	(2 years)	½S d/6 6d/7 ET 2.5% Pa 1 (1)	8/y	2 708^a	1 624^a	85	—	—	1.6	—
AVROS 2037	6	½S d/3 6d/7 ET 5% Ba 2 (2)	4/y	26 723	4 647	100	—	—	16.0	19.4
	(6 years)	½S d/6 6d/7 ET 5% Pa 1 (1)	10/y	21 789^a	3 789^a	82	—	—	7.0^a	10.1^a
PB 5/51	7	½S d/3 6d/7 ET 5% Ba 2 (2)	4/y	19 948	4 987	100	36.5	4.2	—	—
	(4 years)	½S d/6 6d/7 ET 5% Ba 2 (1)	6/y	17 504^a	4 376^a	88	37.1	4.2	—	—

[a]Significantly different from the control at the 0.05 level
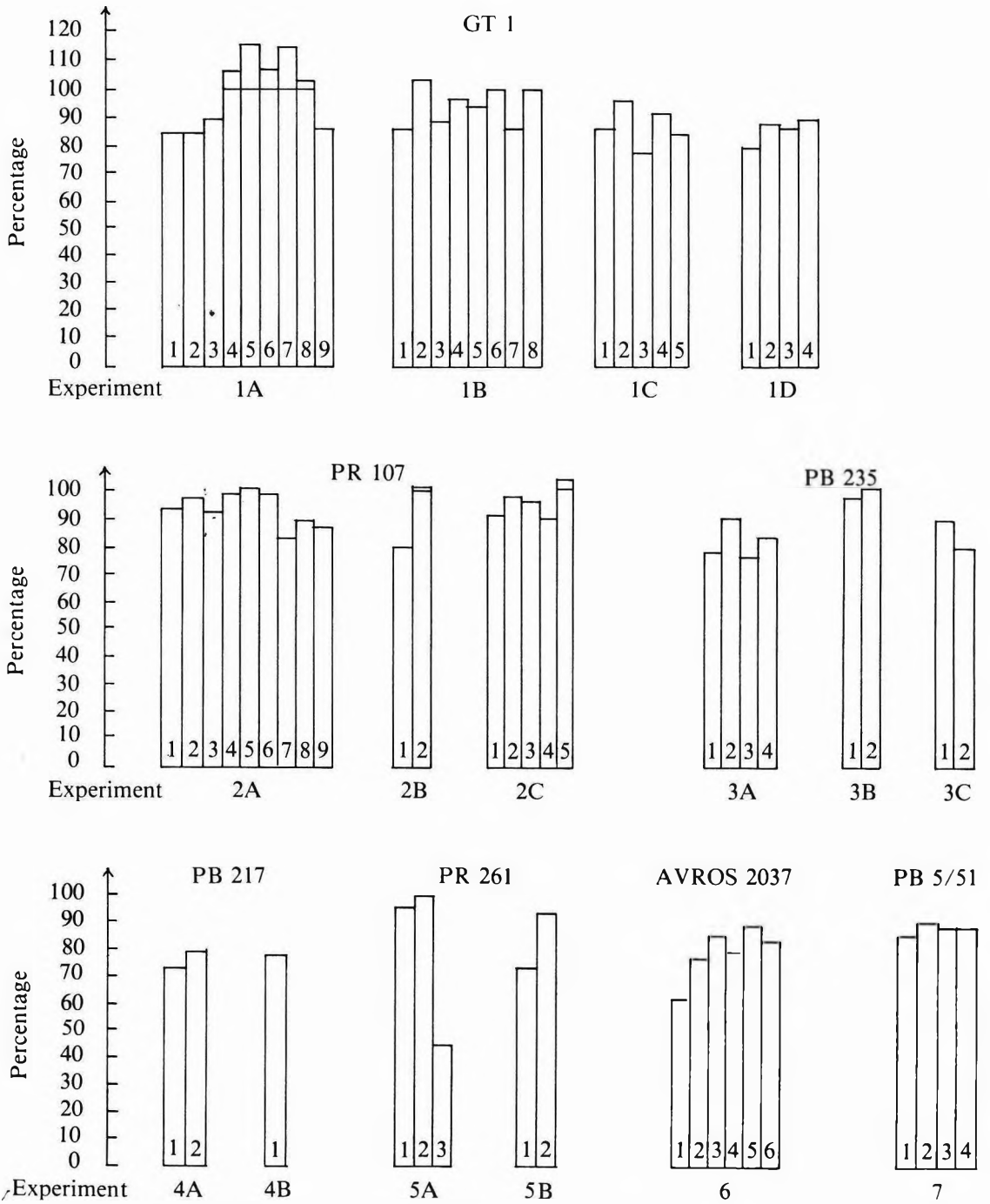
The number at the bottom of each column indicates the number of years after the beginning of the experiment.

Figure 1. Production of weekly tapping (d/6 6d/7) as a percentage of twice-weekly tapping (d/3 6d/7).

higher and amounted to 95% to 96% of that of the control; they were better because the number of stimulations was high. *Figure 1* showed better production of trials on d/7 frequency from the fourth to the eighth year in *Experiment 1A*. The control was at the bottom of the panel while d/7, with a lower bark consumption, was less prone to the phenomenon of panel brake and exhibited better response to stimulation.

During the last trial, upward tapping with ½S on *Panel HO-1* was carried out and the control treatment recovered its advantage.

Latex analyses showed that the percentage of dry extract was usually above that of the control, especially for trees tapped on d/7 frequency which were the least often stimulated. In all the cases, sucrose contents were twice as high as that of trees tapped on d/7 frequency.

It was observed that decreased frequency of tapping had a favourable effect on percentage incidence of dry trees and diseased cut length. On old trees, the percentage was negligible with upward ½S system *(Experiment 1A)* and relatively high with downward ½S system *(Experiment 1B)*.

Clone PR 107

The results of the three experiments carried out on PR 107 *(Table 3* and *Figure 1)* showed that production obtained with ½S d/3 6d/7 was rarely achieved with ½S d/7. A significant effect of the number of stimulations on production was observed over nine years *(Experiment 2A)*.

An effect of the concentration of the stimulant was also observed *(Experiment 2C)*, the best production being obtained with 8% active ingredient. Efficacy was identical with the panel or scraped bark methods of application. With ten annual applications, production obtained with tapping on d/7 was 90% to 97% of that on d/3 6d/7 frequency under four annual stimulations.

Latex d.r.c. were equal to or higher than that obtained with the control. On the other hand,

no significant difference in sucrose contents was observed between the two treatments.

Similarly, the percentage of dry trees or diseased cut length was not affected by decreased frequency of tapping.

Clone PB 235

With clone PB 235, preliminary results obtained *(Table 4* and *Figure 1)* showed a significant effect of the number of stimulations on the production obtained with the ½S d/7 system. With twelve annual stimulations, against two for the control, hardly 82% of the production obtained on d/3 frequency was achieved. When the control was not stimulated *(Experiment 3B)*, four annual stimulations led to a production identical to that of the control.

For treatments on lower frequency, d.r.c. were significantly higher. Sucrose contents were significantly higher than in the stimulated control *(Experiment 3A)* and significantly lower than in the non-stimulated control *(Experiment 3B)*.

Similarly, the percentage of dry trees due to bark dryness and the percentage of diseased cut length were lower for trees tapped on d/7 frequency than for trees tapped on d/3 frequency under stimulation.

Other Clones

Recent experiments on PB 217 showed that the relative production values of d/7 were lower than those of d/3 6d/7 by 80%. Dry extract was significantly higher and sucrose contents were significantly lower. Again, there was a very small percentage of diseased or dry trees *(Table 5)*.

The same applied to PR 261, which seemed ill-adapted to reduced frequencies, especially in the third year of tapping where only 45% of the production of d/3 6d/7 was obtained *(Figure 1)*.

For AVROS 2037, an increase in the relative production value of d/7 was observed compared to the production of d/3 6d/7 which stabilised

around 85% and had a much lower bark dryness rate.

On the other hand, this relative value for PB 5/51 did not vary and amounted to 88%. Latex characteristics were identical for both treatments.

DISCUSSION

Generally, productions obtained with ½S d/7 were lower than those obtained with ½S d/3 6d/7 by 5% to 30%. Despite a higher number of stimulations, it was impossible to offset the decrease in production observed with decreased frequency.

Hevea production depends, on the one hand, on flow duration, which mainly depends on cut length and stimulation, and on the other hand, on latex regeneration capacity between two tappings, which is a function of frequency of tapping.

Without stimulation, the yield in gramme per tapper per tree of trees tapped on d/7 was higher than that of trees tapped on d/3 6d/7[8]. A suitable stimulation, which extends latex flow, should make it possible to obtain a yield identical to that of trees tapped on d/3: the lower the tapping intensity is, the better are the sucrose contents[9] and response to stimulation[10].

For GT 1, the best productions on d/7, compared with those of d/3 6d/7 were obtained on old trees *(Experiments 1A* and *1B)* where the total dose of active ingredient supplied was slightly higher than double of that supplied to the control, contrary to the experiments carried out on trees at opening where the doses supplied were lower.

The best physiological status of the trees tapped on d/7 (higher d.r.c. and sucrose content, lower bark dryness) compared with trees tapped on d/3 6d/7, seemed to indicate that these trees were under-exploited. Some experiments had been altered to obtain a production per tree identical to that of the control.

In the case of GT 1, where panel brake played a major role, production was better

since the tapping cut was supplied with a higher dose of active ingredient. With d/7 frequency, bark consumption was lower than with d/3 6d/7 and the height of renewed bark above the tapping cut was lower. The decrease in production of d/3 was much quicker than that of d/7, leading the latter to a production that was equal or higher than that of d/3 *(Experiment 1A).* This phenomenon disappeared when the tapping cut was under upward tapping or panel upchanging system.

As far as the other clones are concerned, production increased with stimulation intensity. *Figure 2* shows that for all clones, there was a good correlation between the ratios of production and amount of active ingredient supplied on d/7 compared with d/3 6d/7. The amount of active ingredient had to be four times higher on d/7 to obtain a production equal to that obtained on d/3 under stimulation.

Besides increasing production per day considerably, tapping on d/7 also had the advantage of leading to a lower bark consumption, which is appreciably panel-saving. This is particularly important in the case of upward tapping. Panel-saving extends the duration of tapping and allows renewed bark to be less often exploited.

Increased production per tapping, due to extended latex flow, increased the amount of secondary rubber and required more frequent second collections as well as more adaptable collecting containers. The hazards of loss due to rain are also higher. However, the disadvantages that can be solved technically are greatly compensated for by the economic advantages of tapping on d/7.

The choice of a tapping system depends on a compromise between production per hectare and that of productivity per tapper. A high production per hectare will maximise the revenue and a high production per tree and per tapping will minimise the costs. The results of the experiments show that the first objective was achieved with tapping on d/3 6d/7 and the second with d/7.
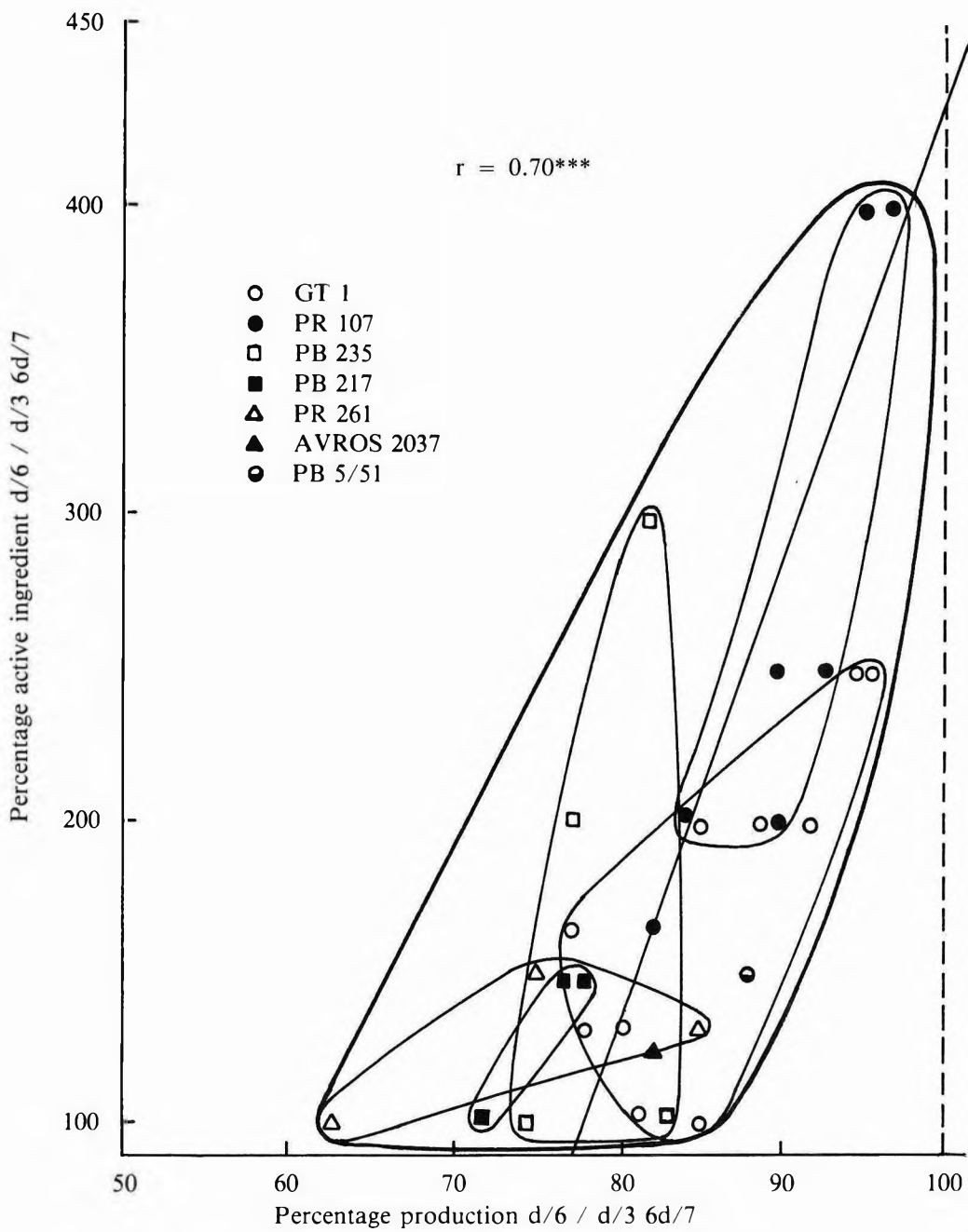
Figure 2. Production and amount of active ingredient supplied by stimulation.
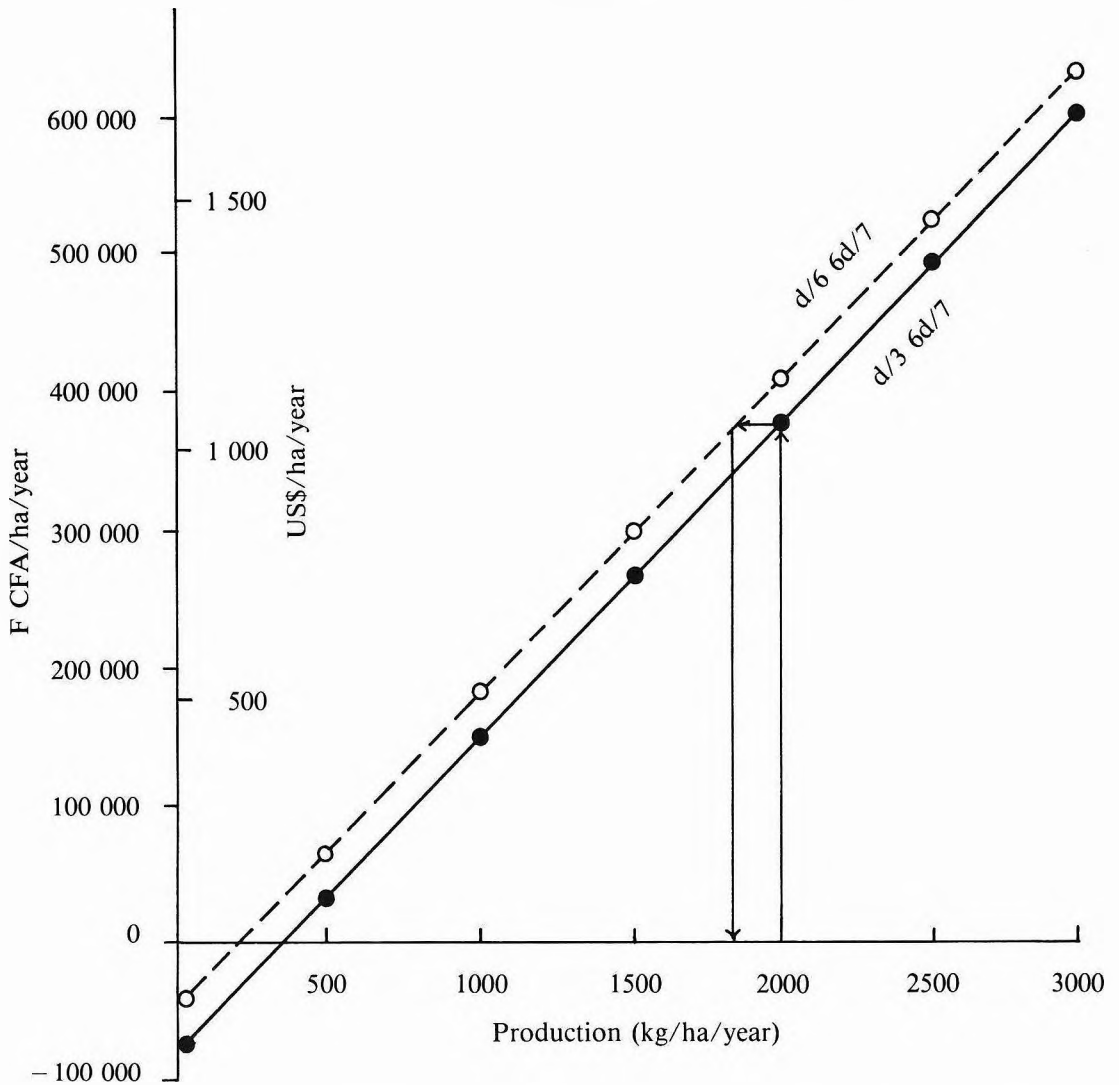
Figure 3. Comparison of profitability of conventional and weekly tapping according to production potential.

This economic study is limited to the case of an existing plantation (where all the infrastructures are established). Revenue *(R)* is dependent mainly on selling price of rubber and costs *(C)* of daily wages *(Appendix B)*.

Figure 3 which compares profitability of tappings on d/3 6d/7 and d/7 according to production potential shows that with 2 *T* per hectare on d/3 6d/7, a minimum of 1.86 *T* per hectare on d/7 is necessary for this system of exploitation to be profitable *(Appendix C)*.

The profitability threshold of d/7 is reached when the difference between revenue and costs is equal for both systems of exploitation. *Figure 4* shows the percentage of production obtained with d/3 6d/7 according to the daily
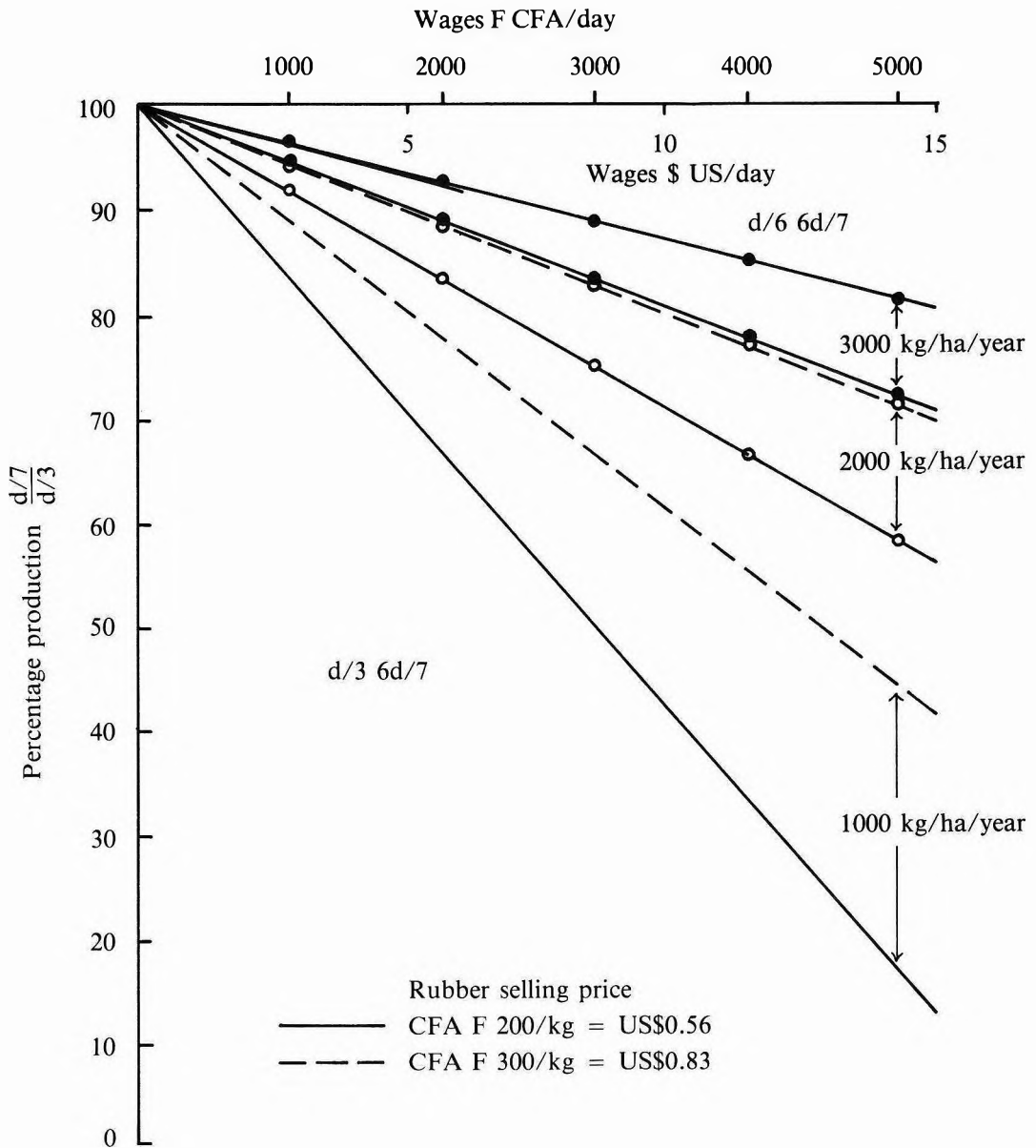
Figure 4. Profitability threshold of weekly tapping (d/6 6d/7) for various production values of conventional tapping (d/3 6d/7) according to the daily wages of one tapper and two hypotheses of prices for the rubber delivered to the factory.

wages of one tapper and to various hypotheses of price for the rubber delivered to the factory to reach the profitability threshold.

The threshold will be easier to reach since the production difference $Y_3 - Y_7$ is large. This production difference increases and the Y_7/Y_3 ratio decreases when the tapper's daily wages increase and the price of rubber decreases.

Figure 4 shows that the higher the cost of labour is, the lower the profitability threshold gets. Thus, with a production of 1000 kg per hectare per year with d/3 6d/7, d/6 6d/7 is more profitable than d/3 6d/7 if its production amounts to at least 83% of the production of the latter, when labour costs are CFA F 1000 per day (*i.e.* US$2.78). If labour cost equals CFA F 3000 (*i.e.* US$8.33), d/6 6d/7 will be more profitable than d/3 if its production amounts to at least 50% of the production of the latter.

The profitability threshold is lower when the price of latex is lower and the more the level of production of d/3 is important, the more important will be the relative production of d/7 *versus* d/3.

In the Ivory Coast the thresholds are 86%, 93% and 95% for yields of 1000 kg, 2000 kg and 3000 kg per hectare per year on the d/3 6d/7 system.

CONCLUSION

Weekly tapping, as currently carried out in the Ivory Coast, does not give the same yield in kilogrammes per hectare as twice-weekly tapping.

Latex properties and tree physiological conditions are better than those obtained with tapping on d/3 6d/7: the trees are under-exploited, as stimulation intensity is not high enough to compensate for the decrease in production due to the reduction in tapping frequency.

The decrease in labour requirements per hectare together with a drop in bark consump-

tion can, under some conditions, make this system of tapping economically more interesting than the conventional one, especially if labour is rare and expensive.

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INTERNATIONAL NOTATION OF TAPPING SYSTEMS

Tapping parameter	Variation in parameters	Significance
Tapping cut	Length	S (full-spiral), ½S (half-spiral),· ¼S (quarter) ...
	Direction	½S ↓ (upward half-spiral)
	Combination of cuts	½S + ¼S ↑ (2 cuts tapped the same day)
		½S, ⅓S ↑ (2 cuts tapped alternately)
Frequency and annual number of tappings	Theoretical	d/3 (tapping every 3 days)
	Practical	d/3 6d/7 (tapping every 3 days out of 6 tapping days a week, *i.e.* alternate frequency 3 days/4 days)
	Periodicity	10m/12 (10 months tapping followed by two months rest)
Panel	Position of the cut on the trunk	H (above the height of opening)
		B (below the height of opening)
	Type of bark	O, I, II (virgin bark, first or second renewed bark)
	Rotation around the trunk	1,2,3,4 (1st, 2nd, 3rd, 4th panel exploited clockwise)
Stimulant	Active ingredient	ET (Ethephon)
	Concentration	2.5% (concentration of active ingredient)
	Amount of mixture	4/2 (4g per tree on a width of 2 cm)
	Application method	Pa (on the panel, above the cut)
		Ba (on scraped bark)
		Ga (on the cut, with removal of lace)
		La (on the cut, without removal of lace)
	Number of stimulations per year and frequency	1/t (once per tapping)
		4/y (4 applications a year)
		12/y (4 w) (12 times a year every 4 weeks)
Particular case of periodic tapping	Number	4: (4 injections per band)
	Placing	PI (on a vertical band)
		PS (on a spiral band)
	Size of the band	50 (2) band of 50 cm in length and 2 cm in width

Example of notation: ½S ↓ d/3 6d/7 10m/12 (2xy) ET 5% Ba 2/2 4/y

Significance: downward half-spiral
tapping every 3 days with 6 working days, *i.e.* d/3 d/4
tapping 10 months out of 12 (with 2 months rest)
annual
ethephon stimulation at 5% active ingredient
application of 2 g of stimulant mixture per tree on scraped bark on a 2 cm band
four applications of stimulant a year.

NET REVENUE PER HECTARE PER YEAR

Net revenue = Gross revenue − Exploitation costs

Gross revenue: $R = Y\,[\,(1 - z)\,(P_1 - a) + zP_2 + d\,]$

   where Y = yield per hectare per year

      z = percentage of lower grades

      P_1 = price of latex grade

      P_2 = price of lower grade

      a = incentive rate for latex

      d = transport costs to the factory

Exploitation costs: Tapping + Stimulation + Second collection cost

$$C = W.\,N.\,\frac{D}{T} + S + B$$

   where W = daily wages (including premiums, social charges, supervision)

      N = annual number of tappings per hectare

      D = density of tappable trees per hectare

      S = stimulation costs per hectare per year

      B = cost of second latex collection

      T = task (trees per tapper)

EXAMPLES OF REVENUE AND COSTS OF WAGES IN THE IVORY COAST

Assuming that:

z	$=$	30%
a	$=$	US\$0.017 per kilogramme dry rubber
d	$=$	US\$0.023 per kilogramme dry rubber
D	$=$	350 trees per hectare
T	$=$	550 trees per tapper
N_3	$=$	104 days for d/3 6d/7
N_7	$=$	52 days for d/6 6d/7
S_3	$=$	US\$18.4 per hectare per year for ET 5% 2 (2) 4/y
S_7	$=$	US\$17.0 per hectare per year for ET 5% 1 (1) 10/y
B_3	$=$	US\$1.75 per hectare per year (d/3, 4 second collection)
B_7	$=$	US\$4.36 per hectare per year (d/7, 10 second collection)

Today for:

P_1	$=$	US\$0.714 per kilogramme and W = US\$2.86 per day
P_2	$=$	US\$0.591 per kilogramme
$R_3 - C_3$	$=$	0.688 Y_3 − US\$209.4
$R_7 - C_7$	$=$	0.688 Y_7 − US\$116.0
$Y_3 - Y_7$	$=$	136 kg per hectare per year
if Y_3	$=$	2000 then Y_7 = 1864 kg per hectare per year

Graft Copolymerisation of Some Hydrophilic Vinyl Monomers in Natural Rubber

H.Y. ERBIL*

Attempts have been made to graft hydrophilic vinyl monomers such as 2-hydroxyethyl meth-acrylate, n-vinyl pyrollidone and methacrylic acid onto natural rubber (NR) using procedures similar to those for grafting methyl methacrylate monomer onto NR latex in order to use the copolymers as a contact lens material. However, these hydrophilic monomers could not be grafted with hydroperoxide-polyamine and ammonium persulphate-sodium meta bisulphite initiator systems due to their high solubilities in the water phase of NR latex.

The monomer, 2-hydroxethyl methacrylate could not be grafted onto dry NR in benzene solution because of its high self propagation tendency. A blend of homopolymers was produced.

The reduction of the pendant methacrylate groups on NR-methyl methacrylate graft copolymer with LiAlH$_4$ in tetrahydrofuran solution introduced hydroxyl groups and hydrophilicity, and reduced the transparency of the reaction product.

Polymers for contact lens applications are often required to possess a spectrum of properties which are not generally found in any one polymer. The five major requirements of a contact lens are transparency, high oxygen permeability, sufficient mechanical properties to resist the deforming force of the eyelid during the blink cycle, wettability by the tear fluid and low protein absorbance[1]. A continuous-wear contact lens can be worn in the eye for successive day and night periods without causing any adverse effect on the eye and it must possess an oxygen permeability coefficient sufficiently high to meet the oxygen consumption rate of the cornea.

Since the copolymerisation provides a balance of the properties of the corresponding homopolymers, the graft copolymerisation would effectively combine the desirable properties of an oxygen-permeable polymer with a hydrophilic monomer in order to produce a contact lens material.

Natural rubber (NR) is chosen for the backbone polymer because of its high oxygen per-meability coefficient[2] [238 $\times$ 10^{-10} cc (STP), mm, cm^{-2}, s^{-1}, cmHg^{-1}] and its appropriate mechanical properties. 2-hydroxyethyl meth-acrylate (HEMA), n-vinyl pyrollidone (NVP) and methacrylic acid are chosen as hydrophilic monomers to graft onto the polyisoprene backbone chain.

HEMA is a suitable monomer for contact lens applications due to its hydrophilicity[3] and polyHEMA hydrogels have been used in biomedical applications since 1960. HEMA monomer has been grafted onto ethylene-vinyl acetate copolymer[4], cellulose[5], silk and wool[6]. PolyNVP has been used as a contact lens material, blood plasma extender and is widely used as a co-monomer for modifying less expensive monomers by enhancing hydro-philicity, improving adhesion properties and increasing softening points of the copolymers. Grafting NVP has been performed by pre-radiation techniques followed by treatment with monomer, whereas other methods involved direct grafting in the presence of azo or peroxide catalysts. NVP has been grafted onto polyacrylonitrile[7], cellulose[8] and nylon[9].

*T.B.T.A.K.-TUGAM-Research Institute for Basic Sciences-Department of Chemistry, P.O. Box 74, Gebze, Kocaeli, Turkey

Grafting methacrylic acid esters, styrene and some other vinyl monomers onto NR has been the subject of a large number of investigations[10-14]. Methyl methacrylate (MMA) grafted NR is a commercial product known as 'Hevea-plus MG' and it is used in solvent adhesives and flexible hard mouldings[15].

This paper discusses the unsatisfactory results[16] of some attempts to graft hydrophilic monomers such as HEMA, NVP and methacrylic acid (MA) onto NR. In addition, grafting MMA monomer onto NR and reducing the grafted methacrylate group by LiAlH$_4$-tetrahydrofuran solution was attempted to enhance the hydrophilicity to the copolymer.

MATERIALS

NR latex containing 62.5% NR was the product of W.M. Symington and Sons Ltd. and it was used as received. MMA, HEMA and NVP monomers were the products of BDH Chemicals Ltd. and they were distilled prior to use. Tert-butyl hydroperoxide, 10% tetraethylene pentamine and MA monomer were the products of Koch-Light Labs. Ltd. and they were used as received.

METHODS

Grafting vinyl monomers onto NR latex with polyamine activated hydroperoxide initiators. In a typical procedure, 30 parts of 2% aqueous NH$_3$ solution was added to 100 parts of NR latex and the mixture was stirred mechanically in a split resin flask at 20°C. 5-30 parts monomer was mixed with 0.18 parts tert-butyl hydroperoxide and 0.3 parts oleic acid and these were added to the NR latex solution with moderately vigorous stirring and the mixture was agitated for 15 min. 0.8 parts 10% tetraethylene pentamine solution was then added to the mixture and stirring continued for a further 10 min. The mixture was left for at least 18 h to permit completion of polymerisation. The product was then isolated by running the latex into at least three times its volume of boiling water containing 0.5% formic acid, the resulting crumb was filtered, washed and dried.

Grafting vinyl monomers onto NR latex with ammonium persulphate-sodium meta bisulphite initiators. 10 parts monomer was added to 100 parts NR latex and the mixture was stirred in a split resin flask for 15 min. 1 part of 12% (NH$_4$)$_2$S$_2$O$_8$ and 1 part of 6% Na$_2$S$_2$O$_5$ (in water) solutions were added to the mixture and stirring continued for a further 15 min. The mixture was then left for at least 12 h to permit the completion of polymerisation.

Grafting vinyl monomers onto NR in benzene solution with benzoyl peroxide initiator. 10 parts monomer solution containing 1% benzoyl peroxide was added to 200 parts 10% NR in benzene solution at 20°C and the mixture was agitated for 15 min. The mixture was then heated to 60°C in 30 min and was kept at this temperature for 8 h.

Reduction of NR-MMA graft copolymer. 5% solution of NR-MMA graft copolymer in tetrahydrofuran was added slowly with vigorous stirring to the 7% solution of LiAlH$_4$ in dry tetrahydrofuran. The copolymer converted into a jelly and was heated at 66°C under reflux for two days. It was then cooled to 0°C by pouring into a mixture of dilute HCl and ice. Sufficient methanol was added until the polymer precipitated and the solution was centrifuged[17]. The insoluble part was separated and dried.

Compression mouldings of the copolymerisation products. The copolymerisation products were mixed with 2% dicumyl peroxide on a two-roll mill. The samples were then compression moulded at 180°C, under 1.4 MPa pressure for 45 min using polished metal plates. Cylindrical thin mouldings were formed.

Fractional precipitation of the copolymerisation products. Fractional precipitation was used to determine the unreacted natural rubber content in the copolymerisation products[18]. Benzene-petroleum ether, 50/50 (60°C-80°C) solution was used to dissolve the products. 1 g of reaction product was left overnight in 200 ml of this solution; it was then stirred at 40°C for 30 min. The undissolved solid content was centrifuged and separated. 20% methanol

(containing 0.01% $CaCl_2$) was added to the remaining solution. The unreacted polyisoprene was precipitated, dried under vacuum and weighed. Percentages of unreacted and reacted NR were calculated. The unreacted polyisoprene film was formed on the cell from $CHCl_3$ solution and the structure of the polymer was identified by IR spectrophotometric analysis using Perkin Elmer Model 457 instrument in order to determine the presence of grafted polymer. The presence of the ester group peak at 1740 cm^{-1} was detected. For MMA grafts, the peaks at 1160 cm^{-1}, 1200 cm^{-1} and 1260 cm^{-1} were also considered.

Contact angle measurements. The contact angle is the angle between the liquid-vapour and liquid-solid interfaces of a drop of the liquid on a solid surface. The contact angle is determined by constructing a tangent to the profile of the drop at the point of contact with the solid surface. Since the tendency for a drop of liquid to spread over a plane surface increases as the contact angle decreases, the contact angle provides a useful inverse measure of hydrophilicity.

Prior to contact angle measurements, the polymer surfaces were cleaned by washing with a detergent solution followed by a thorough rinsing with distilled water and dried. The sessile drop of distilled water was formed on the surface of the polymer through a hypodermic needle. The contact angles were determined directly by using a special low-power microscope as the average of three measurements and reported within a range of ± 1°.

RESULTS AND DISCUSSION

Graft Copolymerisations

The results of graft copolymerisations of vinyl monomers onto NR latex with polyamine activated tert-butyl hydroperoxide initiator and with ammonium persulphate, sodium meta bisulphite initiators are given in *Tables 1* and *2* respectively. The results of the graft copolymerisations of MMA and HEMA monomers onto dry NR in benzene solution with benzoyl peroxide initiator are given in *Table 3*.

In the graft copolymerisation of NR latex, it is necessary that the monomer is absorbed by the rubber particles and the polymerisation takes places within the swollen globules. When MMA monomer was stirred into latex, it first separated into an upper layer, but fairly rapidly, disappeared as a separate liquid phase and soon afterwards no visible separation of monomer occurred on standing. This was due to the slight solubility of MMA in the water phase of latex. However, HEMA monomer has a high water solubility, NVP and MA monomers are also much more water-soluble than MMA and during the course of the copolymerisation, these monomers were homopolymerised in the water phase of the NR latex.

Consequently, as seen from *Tables 1–3,* only MMA-NR graft copolymer was produced in these reactions with used initiator systems. Blends of homopolymers were formed with other vinyl monomer graft copolymerisation attempts. The blends were unsatisfactory for the control of the elastic and hydrophilicity properties of the product.

Ammonium persulphate-sodium meta bisulphite initiator system has lower initiating efficiency than hydroperoxide system and was used for this reason. However, HEMA monomer homopolymerised with this system too. A powerful stabilising system in latex is required, which prevents HEMA monomer dissolving in the water phase of NR latex and which forces HEMA to be absorbed in NR particles. The formation of magnesium hydroxide gel in the water phase of latex may be suggested as a suitable stabilising system for HEMA monomer[19]. On the other hand, the use of the water-insoluble initiator systems may force the monomers to polymerise on the surface of the latex particles.

It was not possible to graft HEMA onto dry NR in benzene solution *(Table 3)* due to the higher rate and the preference of the reaction between HEMA monomer and propagating polyHEMA chain rather than the reaction between HEMA monomer and active species on the NR backbone.

TABLE 1. GRAFT COPOLYMERISATIONS OF VINYL MONOMERS IN NR LATEX WITH
POLYAMINE ACTIVATED HYDROPEROXIDE INITIATOR

Copolymer No.	Parts by weight					Reacted NR (%)	Colour and transparency	Water contact angle (°)	Comments
	NR latex	MMA	HEMA	NVP	MA				
1	100	10	—	—	—	7	Light yellow, transparent	82±1	NR-MMA graft copolymer
2	100	28	—	—	—	19	Light yellow, transparent	77±1	NR-MMA graft copolymer
3	100	15	5	—	—	11	Brown, translucent	79±1	NR-MMA graft copolymer and polyHEMA blend
4	100	—	30	—	—	0	Brown, transparent	74±1	Blend of NR and polyHEMA homopolymers
5	100	—	5	—	—	0	Brown, transparent	76±1	Blend of NR and polyHEMA homopolymers
6	100	—	—	25	—	0	Brown, transparent	78±1	Blend of NR and polyNVP homopolymers
7	100	20	—	—	5	13	Light yellow, transparent	82±1	NR-MMA graft copolymer and polyMA blend

TABLE 2. GRAFT COPOLYMERISATIONS OF MMA AND HEMA MONOMERS IN NR LATEX
WITH AMMONIUM PERSULPHATE, SODIUM METABISULFITE INITIATORS

Copolymer No.	Parts by weight			Reacted NR (%)	Colour and transparency	Water contact angle (°)	Comments
	NR latex	MMA	HEMA				
1	100	10	—	8	Light yellow, transparent	78 ± 1	NR-MMA graft copolymer
2	100	—	10	0	Brown, transparent	76 ± 1	Blend of NR and polyHEMA homopolymers

TABLE 3. GRAFT COPOLYMERISATIONS OF MMA AND HEMA MONOMERS ONTO DRY NR
IN BENZENE SOLUTION WITH BENZOYL PEROXIDE INITIATOR

Copolymer No.	Parts by weight			Reacted NR (%)	Colour and transparency	Water contact angle (°)	Comments
	NR latex	MMA	HEMA				
1	20	10	—	28	Light yellow, opaque	73 ± 1	NR-MMA graft copolymer
2	20	—	10	0	Brown, opaque	79 ± 1	Blend of NR and polyHEMA homopolymers

TABLE 4. REDUCED NR-MMA GRAFT COPOLYMERS BY LiAlH$_4$ IN TETRAHYDROFURAN SOLUTION

Reaction No.	Reduced copolymer	Colour and transparency	Water contact angle (°)
1	Table 1, No: 1	Dark yellow, opaque	76 ± 1
2	Table 1, No: 2	Brown, opaque	73 ± 1
3	Table 2, No: 1	Dark yellow, opaque	75 ± 1
4	Table 3, No: 1	Brown, opaque	71 ± 1

The transparency and colour of the moulded discs depended upon the structure of the copolymerisation products. NR-MMA graft copolymer discs were pale yellow in colour and their transparency decreased with the increase of the MMA content in graft copolymer. The transparency of NR-MMA graft copolymer was a result of both the similarity in the refractive indices (NR = 1.52, PMMA = 1.49) and possible good phase-separation of the long-chain PMMA from the main chain of polyisoprene. The rigidity of the discs increased with the increase in the MMA content.

The water contact angle measurements of the discs showed that there was an increase in wettability of both NR-MMA graft and NR-homopolymer blend products compared with pure NR itself. (The water contact angle of pure NR was 82°). However these products were

found to be too hydrophobic for contact lens applications since the water contact angles of commercial lenses[20] are between 60° and 70°.

Reduction of NR-MMA Graft Copolymer

The results of the reduction of the NR-MMA graft copolymer products by $LiAlH_4$ in tetrahydrofuran solution are given in *Table 4*. The hydrophilicity was increased by the substitution of hydroxyl groups with methacrylate groups as seen in water contact angle results of the graft copolymer discs and confirmed with IR spectroscopy. However the material did not seem to be suitable for contact lens applications since the reduction reaction decreased the transparency of the copolymer. This was due to the fact that, with the reduction of ester group into hydroxyl group, the chemical environment prevented a good phase-separation and since the refractive indices were different from each other, the opaqueness was usual.

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Impact-resistant Polypropylene/Natural Rubber Blends

N.M. MATHEW* AND A.J. TINKER**

It has been demonstrated previously that blends of polypropylene with natural rubber having high impact strength at low temperatures may be prepared by blending in the presence of m-phenylenebismaleimide. The potential for a cheaper additive system, phenolformaldehyde resin with zinc oxide, to replace the m-phenylenebismaleimide has been investigated. The resin and zinc oxide are at least as effective as m-phenylenebismaleimide in increasing both the notched Izod and falling weight impact strength of the blends at low temperatures. Other properties are also generally affected in a similar manner. The effect of the level of resin and zinc oxide on impact strength is considered in terms of the mechanisms leading to increased impact strength, and appropriate levels of resin and zinc oxide are identified. There is a considerable cost advantage in the use of resin and zinc oxide.

The blending of rubbers with polypropylene (PP) to provide improvements in impact strength has been studied widely[1–7], and blends of PP with ethylene/propylene or ethylene/propylene/diene (EPDM) rubbers are produced commercially as impact-resistant PP. Other rubbers have been investigated in this role, including synthetic polyisoprene, though this did not prove to be suitable[7]. There are arguments which suggest that blends of PP and polyisoprene suffer from a lack of interfacial adhesion, which is deterimental to the impact properties of the blend[3]. However, the preparation of blends of PP with natural rubber (NR) possessing good impact strength at low temperatures through blending in the presence of m-phenylenebismaleimide (HVA-2) has been reported[8].

HVA-2 has the potential to combine with both PP and NR radicals produced during mastication to form copolymers capable of promoting good interfacial adhesion between the two phases, and it also crosslinks the NR phase to a low degree. It is known that both of these actions can increase impact strength in rubber-toughened thermoplastics[9]. The relative contribution of the two mechanisms

to the improvement in the impact properties of blends of PP and NR given by the use of additives such as HVA-2 has been considered more recently[10,11], and it has been suggested that the two are complementary though the latter makes the greater contribution provided that the former is also present.

HVA-2 is technically suitable as an additive to promote good impact properties in blends of PP and NR, but the high cost of this material may cause it to be used at a level below the technical optimum. Other potentially suitable additives have been identified[10], including phenolformaldehyde resin with a catalyst to promote crosslinking of the NR phase. The catalyst considered previously was stannous chloride dihydrate, but this compound has some drawbacks, and this communication reports more recent work which has shown that phenolformaldehyde resin activated with zinc oxide is a suitable alternative additive system to HVA-2.

MATERIALS AND METHODS

A viscosity-stabilised grade of NR, SMR CV, was used. Two grades of PP have been con-

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*Rubber Research Institute of India, Rubber Board, Kottayam-686009, Kerala, India
**Malaysian Rubber Producers' Research Association, Brickendonbury, Hertford SG13 8NL, United Kingdom

sidered, one a homopolymer grade (Propathene GWM 22, ICI) and the other a copolymer grade with a flexural modulus of 1400 MPa (Propathene GWM 101, ICI). Both grades of PP have a melt flow index (MFI) of 4 g per 10 min under *Condition L of ASTM D1238.* The HDPE used in ternary blends is a homopolymer with a MFI of 0.75 under *Condition P of ASTM D1238* (Unifos DMDS 5140). Zinc oxide, HVA-2 (DuPont), phenolformaldehyde resin (SP1045, Schenectady-Midland), and the antioxidants (Permanax WSO, Vulnax Int., and Irganox PS800, Ciba-Geigy) were used as supplied.

Blends were prepared in a BR Banbury mixing on a 1 kg scale at a rotor speed of 116 r.p.m. and with steam heating at 0.28 MPa. NR, polyolefin(s) and zinc oxide, when used, were charged into the Banbury and HVA-2 or SP1045 were added after 2 min, following the melting of the PP at 1.5 min. Antioxidants (0.2 p.p.h.p. each of WSO and PS800) were added after 4.5 min, and the batch was dumped after 5 min at a temperature in the range 175°C–185°C. The blends were sheeted on a mill prior to granulation.

MFI were measured at 190°C under a load of 5 kg *(ASTM D1238, Condition P)*. Die swell was measured on the cold extrudate from the MFI test. Izod impact testing was performed on injection-moulded, BS-notched test-pieces in the temperature range −50°C to 23°C. Instrumented falling weight impact testing was performed over the same temperature range on injection-moulded discs 60 mm in diameter and 1.5 mm in thickness using a support diameter of 50 mm and a hemispherical-nosed dart with a diameter of 12.5 mm. The drop height was 50 cm, and the energy available to rupture the test-piece was 65 J. The impact force/time curve was collected, and allowance was made for the slowing of the dart during impact in the calculation of energy absorbed by the test-piece. The falling weight impact strength is given by the energy absorbed to failure of the test-piece. The tensile properties of the blends were measured on dumbbell test-pieces with a gauge length of 12.5 mm cut from the injection-moulded discs. The measurements were made

at 23°C using an Instron tensometer operating at a crosshead speed of 50 mm per minute.

RESULTS

Two series of blends containing 15% NR have been considered, binary blends of a homopolymer grade of PP with NR and ternary blends comprising a copolymer grade of PP, NR and HDPE. Each series includes a blend prepared in the absence of additives and a blend prepared in the presence of HVA-2 in addition to the blends prepared with various levels of phenolformaldehyde resin and zinc oxide *(Tables 1* and *2)*. In accord with previous reports[8,10,11] the use of these additives in the preparation of the blends caused a marked reduction in the MFI of the blend *(Tables 1* and *2)*. Die swell during the MFI test tended to be reduced by the additives, a reflection of crosslinking of the NR phase[10,11].

The notched Izod impact strength of the binary and ternary blends are presented as functions of temperature in *Figures 1* and *2* respectively. The addition of HVA-2 to either of these types of blend gave the expected increase in impact strength. The phenolformaldehyde resin/zinc oxide system was at least as effective in increasing notched Izod impact strength. In the binary blends, the resin and zinc oxide are more effective and impact strength is higher at the higher level of resin. The effect of level of zinc oxide on impact strength is not marked. In the ternary blends, there is no consistent difference between the efficacy of the two additive systems over most of the temperature range in which failure occurred, and neither the level of the resin nor the level of the zinc oxide exerts a consistent effect within the limits considered here.

The falling weight impact strength of the ternary blend at low temperatures is increased by the addition of HVA-2 *(Table 3)*, as reported previously[10,11]. The phenolformaldehyde resin with zinc oxide is also effective in increasing falling weight impact strength, despite the presence of the particulate zinc oxide. As with notched Izod impact strength, there is little consistent difference between the abilities of the additive systems to increase falling weight

TABLE 1. PROPERTIES OF 15 : 85 NR: HOMOPOLYMER PP BLENDS

Item	Blend No.					
	1	2	3	4	5	6
Additives (p.p.h.p.)						
HVA-2	—	0.5	—	—	—	—
SP1045	—	—	1.0	1.0	2.0	2.0
ZnO	—	—	0.5	1.0	0.5	1.0
Properties						
MFI (g/10 min)	8.7	0.67	0.49	0.30	0.66	0.42
Die swell (%)	70	70	38	38	31	28
Yield stress (MPa)	24	25	23.8	24.5	24.2	24.2
Yield strain (%)	16	13.5	16	13.5	12.5	14.5
Tensile strength (MPa)	28.2	29.1	33.9	34	35.1	34.5

TABLE 2. PROPERTIES OF 15 : 75 : 10 NR : COPOLYMER PP : HDPE BLENDS

Item	Blend No.					
	7	8	9	10	11	12
Additives (p.p.h.p.)						
HVA-2	—	0.5	—	—	—	—
SP1045	—	—	1.0	1.0	2.0	2.0
ZnO	—	—	0.5	1.0	0.5	1.0
Properties						
MFI (g/10 min)	8.6	1.2	0.71	0.41	0.16	0.17
Die swell (%)	63	47	66	47	23	17
Yield stress (MPa)	18.4	19.8	19.6	19.3	19.6	19.8
Yield strain (%)	20.5	15.5	17	17	16.5	16.5
Tensile strength (MPa)	25.4	29.7	30.4	30.2	31	30.9

impact strength at these low temperatures, although the blend containing the highest level of resin and zinc oxide generally has the highest impact strength.

Only HVA-2 gave a significant increase in the yield stress of the binary blend based on a homopolymer grade of PP, which was evident in earlier work on binary blends based on the copolymer grade of PP[8] *(Table 1)*. Yield strain is reduced by both types of additive, and tensile strength is increased markedly, in accord with previous experience. The ternary blends based on the copolymer grade of PP do show an increase in yield stress due to both types of additive, in addition to the reduced yield strain and higher tensile strength *(Table 2)*.

DISCUSSION

A reduction in MFI of a blend due to the presence of additives during the preparation has been associated with one mechanism of increasing impact strength, increased interfacial
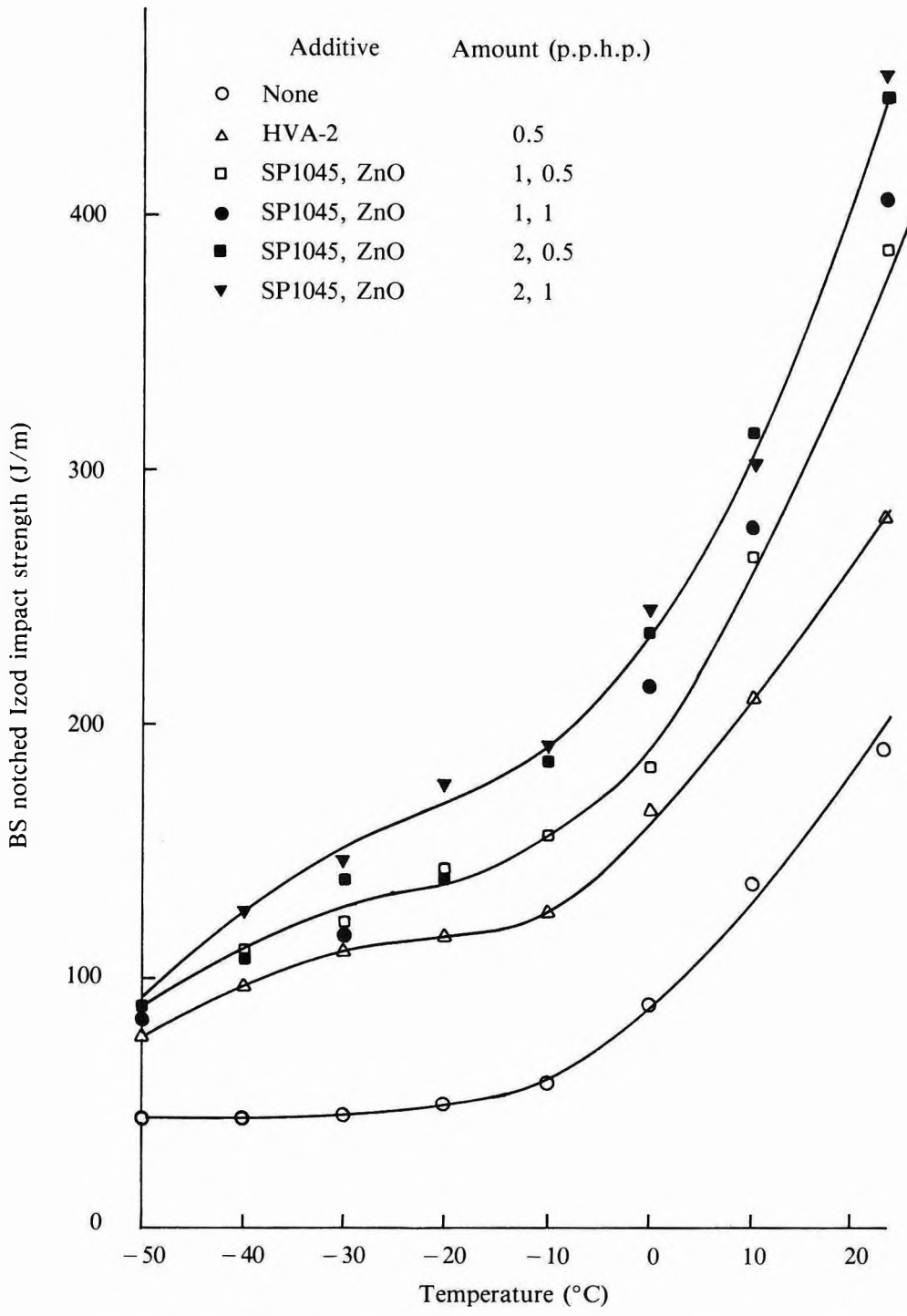
Figure 1. BS notched Izod impact strength of 15:85 NR: homopolymer PP blends as a function of test temperature, showing the effect of HVA-2 and resin/zinc oxide.
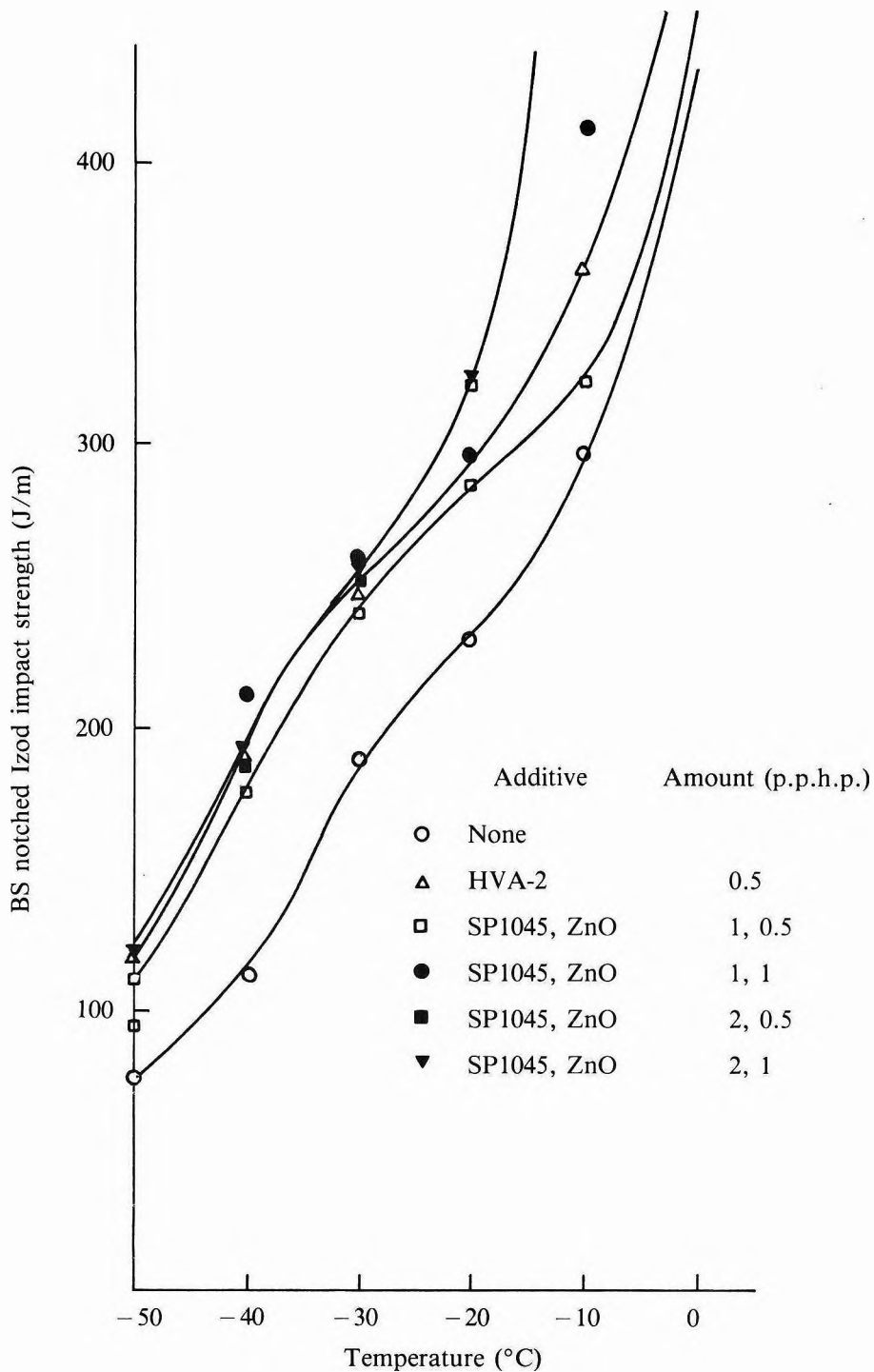
Figure 2. BS notched Izod impact strength of 15:75:10 NR: copolymer PP: HDPE blends as a function of test temperature, showing the effect of HVA-2 and resin/zinc oxide.

TABLE 3. FALLING WEIGHT IMPACT STRENGTH OF 15 : 75 :10 NR : COPOLYMER PP : HDPE BLENDS

Blend No.	Falling weight impact strength (J)		
	$-20°C$	$-35°C$	$-50°C$
7	11.7	12.8	8.6
8	11.8	14.3	13.3
9	12.1	12.1	13.3
10	12.8	14.2	13.7
11	12.5	14.3	13.1
12	12.8	15.0	14.2

adhesion. A reduction in die swell is associated with another mechanism, crosslinking of the NR phase. The maximum benefit in terms of impact strength is realised when both mechanisms are operating.

Some care must be exercised in relating impact strength and die swell, since there are competing effects. Additives which increase interfacial adhesion without crosslinking the NR phase cause an increase in die swell[10,11]. The die swell of a blend prepared in the presence of an additive which increases interfacial adhesion and causes crosslinking of the NR is therefore affected by both of these processes, and it is not a simple reflection of the degree of crosslinking. However, the Izod impact strength of the binary blends does correlate with the die swell of the blends, which increases with increasing level of resin and is greater for the blends containing the resin than the blend containing HVA-2.

Such discrimination between the two additive systems and the effect of crosslink density, as indicated by die swell, is not readily evident in the Izod impact strength of the ternary blends. However, it has been demonstrated that the effect of crosslinking the NR phase on the Izod impact strength of a blend is most marked at temperatures above about $-30°C$ to $-20°C$[10,11], and this is also apparent for the binary blends considered here. The high impact strength of the ternary blends curtailed the temperature range over which it was measured, and for the majority of that range

there is little consistent difference between the blends. Nonetheless, the limited data available above $-20°C$ are in accord with a higher impact strength at a higher level of crosslinking, as indicated by a lower die swell.

It has been shown that, in common with other rubber-modified thermoplastics[12], there is an optimum degree of crosslinking of the NR in blends with PP above which impact strength decreases[10,11]. Given that the difference between the Izod impact strengths of the blends containing 1 p.p.h.p. and 2 p.p.h.p. resin is not large, the optimum level of crosslinking is probably achieved with a resin level close to 2 p.p.h.p.

It is not unusual for two such different measures of impact strength as notched Izod and falling weight to give different relative assessments of a number of materials. However, in this instance the falling weight impact strengths of the ternary blends present a similar assessment of the effect of the additives as notched Izod impact strength. Both additive systems increase the falling weight impact strength of the blend at low temperatures, and there is little consistent difference in the increase provided by the two additives or by the two levels of resin. The additives not only increase the falling weight impact strength of the blend, the ductile-brittle transition temperature is also reduced. The latter parameter is defined as the highest temperature at which the energy absorbed to failure is coincident with the energy absorbed to peak load during impact. The ductile-brittle transition temperature of the blend without additives[7] is close to $-50°C$, since the energy absorbed to peak load is 8.45 J. The falling weight impact strengths at $-50°C$ of the blends prepared in the presence of additives are well in excess of the energies absorbed to peak load, which all lie between 9.16 J and 9.23 J, and the ductile-brittle transition temperatures for these blends are therefore below $-50°C$.

From a practical viewpoint, the marked reduction in the MFI of a blend caused by the additives may seem disadvantageous, since it suggests a substantial reduction in processability.

However, it has been shown that the MFI of a blend prepared in the presence of HVA-2 is not a reliable indicator of processability — the viscosity of the blend is only slightly increased by the additive at the high shear rates prevailing in processing by injection moulding[8].

CONCLUSIONS

Phenolformaldehyde resin with zinc oxide is effective in increasing the impact strength of NR/PP blends at low temperatures, when added during the preparation of the blends. Both notched Izod impact strength and falling weight impact strength are increased, and the ductile-brittle transition temperature in the latter test is reduced. In the practically more interesting ternary blends, the resin and zinc oxide increase yield stress and tensile strength. The resin with zinc oxide could replace the more expensive HVA-2 as an additive and, given the relatively small differences observed between the two levels considered here, 1 p.p.h.p. of resin with 0.5 p.p.h.p. zinc oxide is adequate. At current prices, this represents a reduction in the cost of the additive of about 75%.

ACKNOWLEDGEMENT

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Surface Friction of Epoxidised Natural Rubber in Its Raw State

E.L. ONG* AND A.D. ROBERTS**

Measurements of the sliding friction of unvulcanised samples of various grades of epoxidised natural rubber have been made against steel over a wide range of speed and temperature. Some steel tracks were deliberately roughened to find what difference this caused. The effect of polymer blending on friction and the role that plasticisers can play in reducing the surface friction were investigated in relation to practical matters.

In view of the promise of epoxidised natural rubber (ENR) as a new polymer[1], the frictional behaviour of the unvulcanised material has been investigated in a series of simple experiments aimed at an understanding of interfacial events during sliding on a steel substrate. The variation in glass transition temperature afforded by different degrees of epoxidisation bears directly upon frictional behaviour. It is of scientific interest to see whether the variation in glass transition temperature can be used as an alternative to different operating temperatures in order to construct a friction 'master-curve'. A study of the friction of ENR grades is of technological interest because it will help to foresee the process behaviour of the raw polymer in factory operations.

EXPERIMENTAL

Rubber samples were designated grades of Standard Malaysian Rubber (SMR) and ENR[1]. All were masticated down to a common Mooney viscosity of 60 ± 2. The masticated samples were compression-moulded into hemicylinders, the cavity mould surfaces being smooth and bright. Mould times were 30 min–60 min at temperatures of 110°C–120°C. Hemicylinders were left to cool in their moulds under pressure and, apart from highly epoxidised grades, they were removed without the need for release agents. For ENR-50 and ENR-70, which are moderately tacky, moulding was done against a Melinex sheet placed in the mould cavity. When these samples were to be tested the Melinex was peeled away from the cylindrical test surface. All the hemicylinders had a radius of curvature of 21 mm and axial length of 15 mm. In this raw state (no compound ingredients and unvulcanised), the hemicylinders were friction tested.

The majority of the friction measurements were made using apparatus that has been described in an earlier communication[2]. Some additional low temperature measurements were made in a deep-freeze cabinet[3]. Raw rubber hemicylinders were pulled over a smooth steel plate track under a fixed normal load of 4.5N. Sliding speeds were varied between 0.001 mms⁻¹ and 100 mms⁻¹ and the steel track surface temperature could be raised to 80°C by an electric hot plate placed under it. For each friction measurement, a rubber hemicylinder sample was brought into loaded contact with the steel track for at least 2 min dwell, the rubber side profile viewed and measured to find the width of the contact band, and then pulled. The contact width was most easily measured by inserting Melinex 'feelers' into either side of the contact region and recording their separation against a ruler, typical contact band widths being 7 mm to 12 mm. At temperatures of 50°C and higher, a longer dwell time of 5 min was allowed so that the rubber surface was brought to full temperature before sliding was initiated.

*Rubber Research Institute of Malaysia, P.O. Box 10150, 50908 Kuala Lumpur, Malaysia

**Malaysian Rubber Producers' Research Association, Brickendonbury, Hertford SG13 8NL, United Kingdom

RESULTS

Friction of ENR-50

Experiments were carried out with raw ENR-50 hemicylinders at temperatures of 25°C, 55°C and 80°C and data were plotted as the variation in friction coefficient, μ (friction force F/normal load W) with sliding speed *(Figure 1)*. The data show some dependence on temperature. At higher sliding speeds and lower temperatures there was a tendency to stickslip motion *(Figure 1* shows highest and lowest values of coefficient), with only slight scuffing of the rubber surface. At low sliding speeds and high temperature, motion was continuous, with material transfer to the steel track. At intermediate speeds and temperature, ridges[2] formed on the rubber surface and rolls of debris were left on the steel track.

Friction of Various ENR Grades

Friction measurements were made for different levels of sample epoxidation from zero (SMR-L) to 70 mole per cent. Despite scatter, differences in behaviour can be discerned *(Figure 2)*. In general, for a given temperature and speed, the sliding friction increases with the extent of epoxidation, and the more highly epoxidised samples had a greater tendency to stickslip motion. For low epoxidisation gross ridge formation on the sample surface often occurred, whereas at high epoxidation tiny surface cracks were observed. These cracks may reflect a lower tear strength[4].

Master-curve of Friction Data

Using the WLF equation[5] an attempt was made to transform the coefficient of friction data *(Figures 1* and *2)* into a single 'master-curve'[6]. The glass transition temperature *(Tg)* of the SMR-L sample was $-70°C$, and each mole per cent epoxidation raised the glass transition by one degree (all values determined by differential scanning calorimetry). Friction transforms were plotted with the experimental Tg values inserted into the WLF equation. The exercise was only partially successful in that the data did not pull together into a clearly defined

master-curve. However, if allowance was made for the area of rubber surface observed to be in contact with the steel plate, matters improved.

The contact width made between rubber and steel was measured for every test run (see above), and from this the contact area was estimated (contact width × hemicylinder axial length). The area varied with temperature and grade of ENR. The area estimates were used to calculate friction shear stresses (friction force/contact area), and when these stresses were plotted against the reduced sliding speed $a_T V$ (a_T is the WLF transform factor) the data points were tightened into a 'master-curve', with a further improvement *(Figure 3)* coming from multiplying the shear stress by Ts/T, where $Ts = Tg + 50$, since forces in polymer chains depend upon the absolute temperature. The master-curve *(Figure 3)* shows a steady rise in friction stress with rate until the parameter $a_T V$ reached values around 4 when considerable macro-stickslip was encountered. At even higher a_T values the friction declined to a small steady value equivalent to $\mu = 0.3$, not unlike the level of friction found for plastics materials such as polystyrene, PMMA, PVC[7]. At this low level of friction all signs of stickslip motion disappeared. To reach the high $a_T V$ values meant that the ENR samples had to be cooled below 0°C, and it was found that under these conditions the sample material was hard and only suffered slight wear during sliding. The minimum temperature at which ENR-50 and ENR-70 were tested was $-33°C$, which implied lg $a_T V$ values as high as 39 when the sliding speed was 10 mms^{-1}. Out to such high $a_T V$ values the friction continued to remain low ($\mu \approx 0.3$) and constant for all speeds tested (0.1 – 10 mms^{-1}).

It is noted that the results presented in *Figure 3* were obtained from two distinctly different pieces of apparatus; at 25°C and above from an apparatus[2] placed on an open bench, at 0°C and below from an apparatus[3] placed in a deep-freeze cabinet. Although there was some scatter, which is to be expected, it is encouraging to see the agreement between data from the two apparatuses.
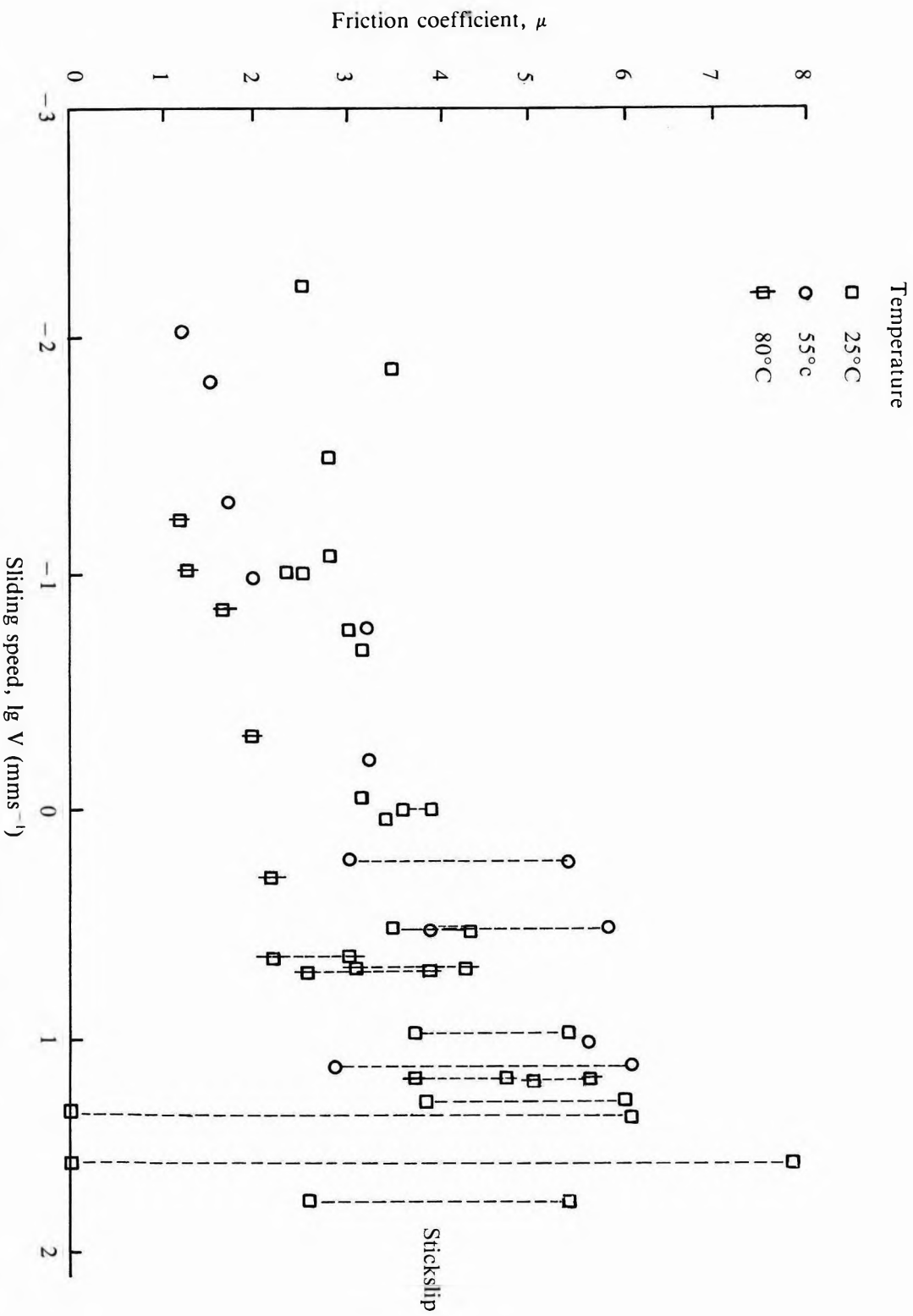
Figure 1. Friction dependence on sliding speed for hemicylinders of ENR-50 slid on a smooth steel track (0.06 μm CLA) at different temperatures. RH = 55%-65%, normal load 4.5N.

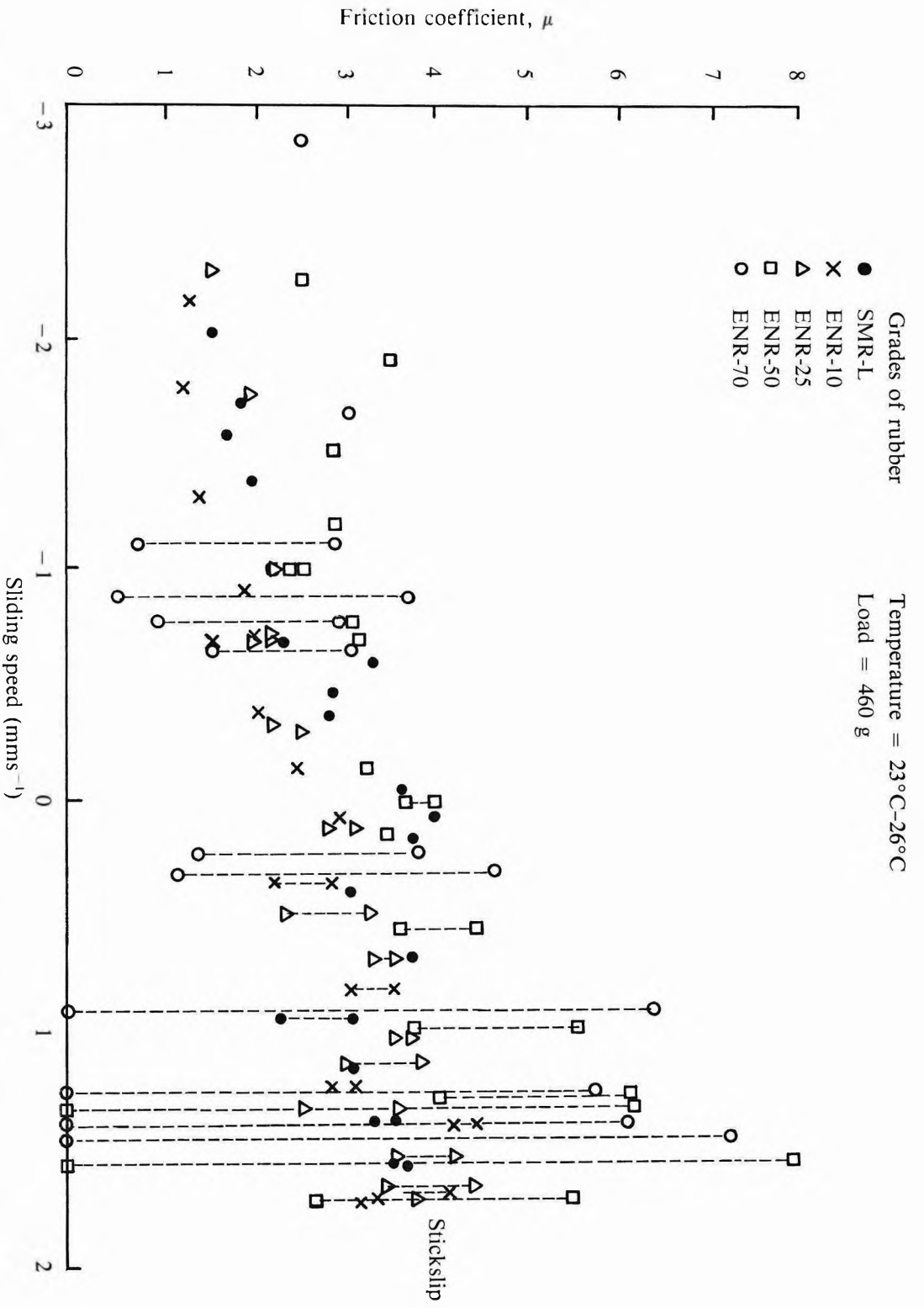Figure 2. Friction dependence on sliding speed for hemicylinders of SMR-L and four grades of ENR slid on a smooth steel track (0.06 μm CLA). Temperature = 23°C–26°C, normal load 4.5N, RH = 55%–65%.
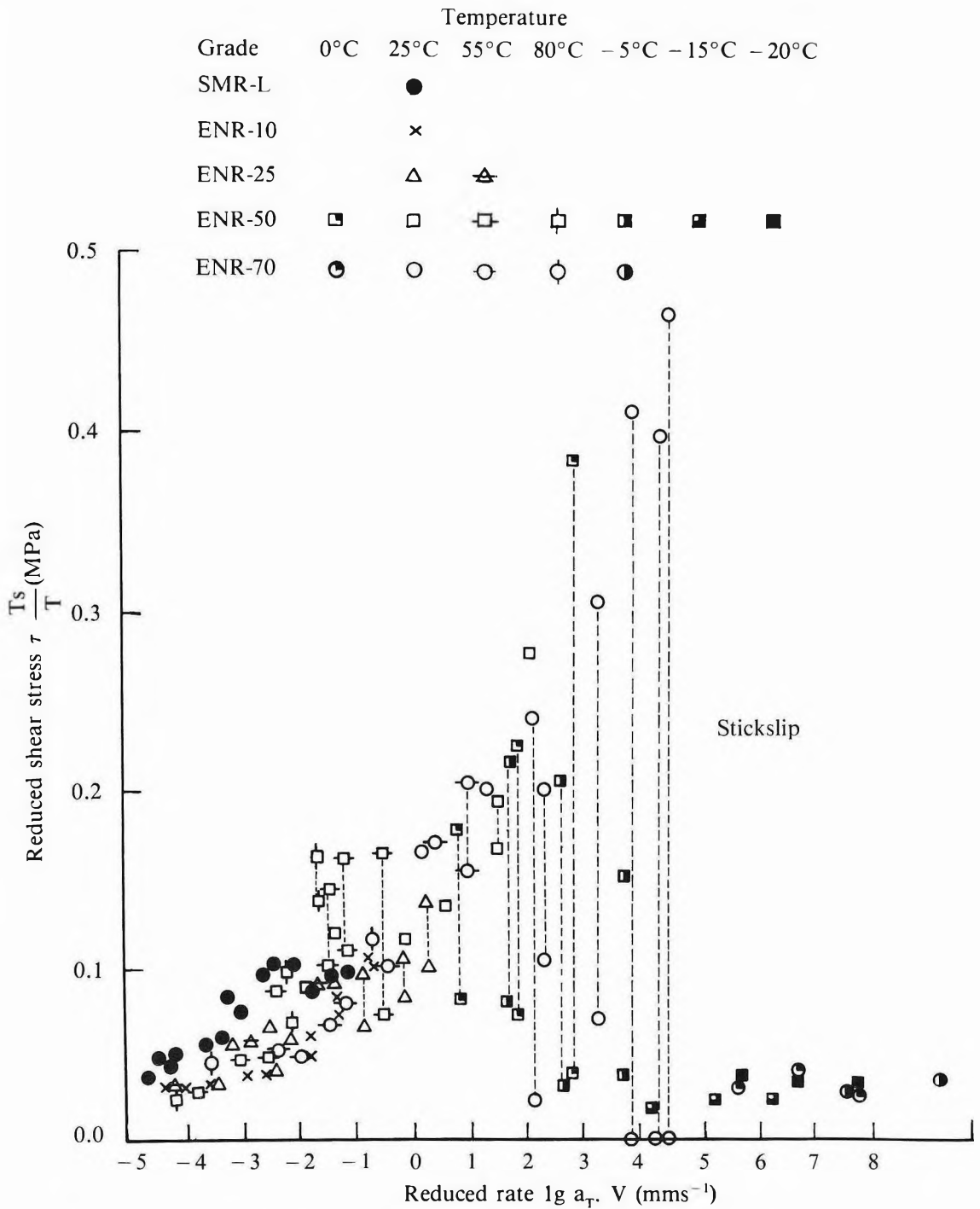
Figure 3. Effect of temperature and speed on interfacial shear stress for hemicylinders of SMR-L and different grades of ENR slid on a smooth steel track (0.06 µm CLA). Normal load 4.5N, RH = 55%-65%.

Influence of Surface Roughness

The effect of different degrees of track surface roughness on the friction coefficients of ENR-50 was investigated at a sliding speed of 1 mms^{-1}, using friction apparatus housed in a temperature cabinet[3]. This equipment allowed for more accurate force measurements and closer control over environmental conditions: the result was generally less scatter in the friction data. Roughening of a track was carried out with aluminium oxide and silicon carbide papers, and the resulting track roughness measured with a 'Talysurf' stylus profilometer.

It was found that the friction was higher on a slightly roughened track when compared to smooth or very rough tracks *(Figure 4)*. This is similar in trend to other observations[2,8]. Measurements carried out at elevated temperatures of 55°C and 80°C also showed a similar increase in friction level on a slightly rough surface *(Figure 4)*.

It is noted that the smoothest surface used to obtain friction/roughness data *(Figure 4)* was chrome-plated steel, its measured roughness being 0.02 μm CLA. All other surfaces were roughened mild steel. A supplementary experi-
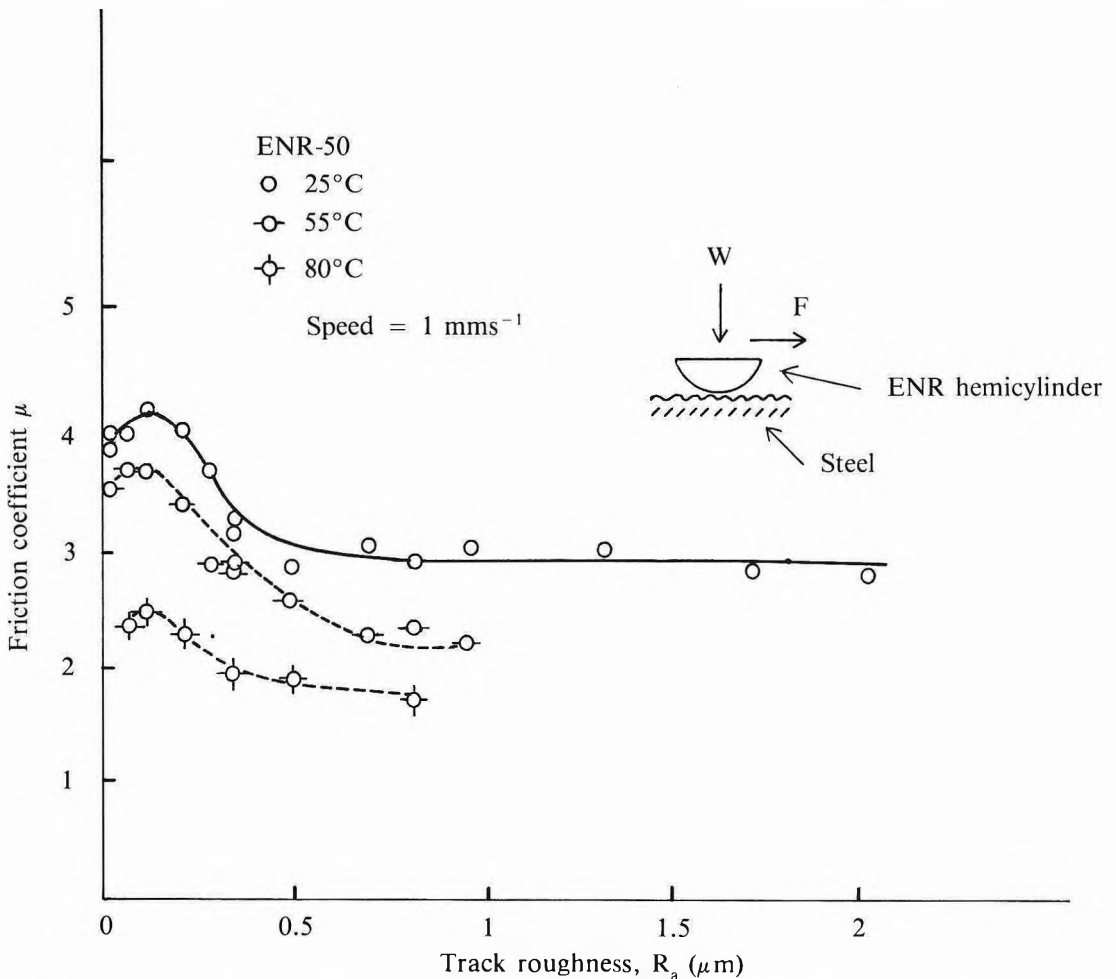

Figure 4. Friction of ENR-50 hemicylinders on steel tracks of different surface roughness maintained at different temperatures. Speed 1 mms^{-1}, normal load 4.5N, RH = 55%–65%.

ment was carried out in which an ENR-50 hemicylinder was drawn over silicon carbide paper that had an approximate roughness of 30 μm. It was interesting to find that the friction coefficient on this paper was $\mu = 3$, in line with the values at roughness of 1–2 μm.

The hemicylinders were examined visually after sliding against a roughened surface. At low roughness (less than 0.5 μm) a rubber ridge was always formed on the hemicylinder. With increasing roughness there was less rubber deformation into a ridge because the extended real area of contact was broken up into a series of point contacts. This led to 'pitted' abrasion patterns and no ridge formation at the higher roughnesses investigated. The patterns appeared to be formed by a combination of tearing[4] and yielding.

ENR Blends

Suitable amounts of unmasticated ENR-50 and SMR-L were mixed together on a two-roll mill to produce blends of Mooney viscosity ≈ 60 containing 25% and 10% levels of epoxidation, and then the friction values of these blends were measured. It was found that the friction levels of blends were comparable to that of ENR containing the same amount of epoxidation *(Table 1)*. Although only speculative, it was

noticed that by using the empirical equation:

$$\mu_{\text{blend}} = \mu_A n_A + \mu_B n_B$$

where μ_A and μ_B are the friction coefficients

n_A, n_B are the mass fractions of the unmasticated component materials,

a reasonable estimate of the blend friction could be made *(Table 1)*. However, the blend friction may also be influenced by factors such as the extent of mastication and the stability of the component materials during blending. Also, the scatter in the friction data means some uncertainty in the argument for this simple law of mixtures, but it is offered as a thinking point.

Plasticisers as Surface Lubricants

Two commercial grades of plasticisers, namely Struktol A-60 and Struktol WB-16 (undisclosed mixtures of metal soaps of high molecular weight fatty acids, made by Schill and Seilacher) were evaluated for their influence on the surface friction of epoxidised natural rubber. They were cast from a volatile solvent onto the metal track. Typically it was observed that a 20%–25% reduction in friction level for rubber/metal contacts was achieved at room temperature. Lubrication was more effective at temperatures approaching the melting range of the plasticisers, the reduction in friction level being about 70% at 80°C *(Table 2)*.

TABLE 1. FRICTION OF ENR AND ITS BLEND WITH SMR-L

Grade/Blend	Friction, μ at different sliding speeds, V		
	0.2 mms^{-1}	0.7 mms^{-1}	1.3 mms^{-1}
ENR-25	2.1	2.6	2.9
ENR-50/SMR-L (1/1)	2.3	2.6	2.8
1/1 Blend estimate	2.3	2.6	3.2
ENR-10	1.8	2.5	2.9
ENR-50/SMR-L (1/4)	2.1	2.6	2.8
(1/4) Blend estimate	2.3	2.6	3.0
SMR-L (unmasticated)	2.3	2.7	2.9
ENR-50 (unmasticated)	2.2	2.6	3.5

Rubber hemispheres sliding on metal track under 4.5N load. Temperature 23°C–25°C, RH = 55%–65%.
Friction quoted were average values; the scatter was about 20%.

TABLE 2. EFFECT OF PLASTICISERS ON ENR (BLENDED)

Plasticiser applied	Temperature (°C)	Friction coefficient	Observations
No plasticiser	25	2.6	Single ridge formed
	80	2.0	Transfer
Struktol A-60 film	25	2.0	Single shallow ridge
from toluene	80	1.1	Tearing and transfer, no plasticiser accumulation
Struktol WB-16 film	25	2.0	A thin layer of plasticiser film swept
(cast from ethanol)	80	0.9	off by the specimen
Mould release agent	25	<0.1	No apparent surface damage
(Addison Chemicals)	80	0.9	
Soap solution	25	0.3	No apparent surface damage
(10% Teepol)	80	0.1	

Sliding speed 0.2 mms^{-1}, load 4.5N, RH = 55%–65%. Average values of friction quoted, scatter 20%. 1/4 Blend ENR-50/SMR L.

When an excess amount of a mould release agent (Bomb-Lube, Addison Chemical) was sprayed onto the metal track at 25°C the sliding friction was reduced to almost zero. Partial evaporation of the volatile solvent in the mould released agent at 80°C led to an increase in the coefficient of friction to about 0.9.

Soap solution (10% Teepol) was found to be a very effective surface lubricant which reduced the coefficient of friction of a metal/ENR contact to 0.3 and 0.1 when measured at 25°C and 80°C respectively. Concomitant with this is a reduction in surface damage of the rubber specimen.

DISCUSSION

Both the temperature and level of epoxidation were found to influence the surface friction of raw ENR, but for any meaningful comparisons to be made it was necessary to take account of the sliding contact area as measured directly in the experiments. It then becomes possible to transform friction shear stress data into a single 'master-curve' by using the WLF equation. The added feature, compared to earlier published data[2] for SMR-CV, is that high values of the reduced rate parameter could be reached by using epoxidised rubber samples. The resulting master-curve resembles those[6,9] for vulcanised rubber. However, in making the comparison, certain differences are noted. For operating conditions adjacent to the glassy region very severe stickslip is encountered (Figure 3, centre); usually this arises if friction has a negative dependence on velocity, and in this case is presumably enhanced by the tackiness of the ENR. For conditions of high temperature/low speed (Figure 3, left hand side), the frictional stress is very low and becomes vanishingly small with decreasing rate. Here, presumably, the resistance to motion is mainly viscous. This behaviour may be contrasted with vulcanised rubber where it is believed that the more elastic-like material gives rise to a true static friction[10].

The enhanced friction at low surface roughness (Figure 4) is similar in trend to some observations[2,8] made with SMR-L and RSS 1, but the point to note, at least for ENR-50, is that the maximum largely occurs in the roughness range 0.1-1 μm CLA. This range is of technological interest. When processing raw

rubber typical examples of surface finish encountered would be 0.8 μm CLA for the screw and barrel in an extruder, and 0.05–0.2 μm for CLA for well polished rotor surfaces in an internal mixer. The study here suggests that in this range the friction could nearly double with changes in surface roughness.

It is foreseen that there will be a need to blend ENR with NR for some applications, such as in tyre building, tyre tread formulations and engineering components. An understanding of the likely level of friction when processing such blends will be of benefit.

Process trials with ENR have shown that sticking problems can occur. For example, in mill mastication there appears to be safe temperature limits above which particular grades of ENR will start to stick onto the roller surface. The addition of certain accelerators to the raw rubber can ameliorate the problem. Plasticisers, such as zinc stearate, can also overcome the problem and hence a study of their lubricity for raw rubber/metal substrate contacts is of direct practical interest. Our studies *(Table 2)* clearly indicate that some materials are only effective at high temperatures, above their melting point, whereas others depend upon a different mechanism and become poorer lubricants at high temperatures.

CONCLUSION

The friction of raw ENR grades broadly varies according to glass transition temperature and, in common with other rubbers, according to ambient temperature and surface sliding speed. Data for various grades can be transformed into a single rate-temperature 'master-curve'. At low rates the frictional behaviour is akin to interfacial viscous shear with no true static friction, at intermediate rates stickslip motion tends to be present and at high rates 'glassy polymer' type friction ensues. Against slightly rough steel the friction can be greater than for

a bright smooth finish or a grossly rough one. A simple prediction of the friction of NR/ENR blends seems possible for practical purposes and there is evidence for the action of plasticisers as surface lubricants.

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Thermal Oxidative Ageing of Epoxidised Natural Rubber

ABU BIN AMU*, ABDUL RAHMAN BIN RAIS* AND SIDEK BIN DULNGALI*

Retention in tensile property of epoxidised natural rubber (ENR) vulcanisate obtained after being subjected to thermal oxidative ageing is determined by the net result of the softening and hardening effects. These softening and hardening phenomena occur during the ageing process.

Three types of fillers, namely HAF black, local clay and silica were investigated to observe the differences in the extent of hardening imparted by these fillers after ageing for three days at 100°C. Of the three fillers investigated, silica-filled ENR-50 (ENR with 50 mole per cent epoxidation) vulcanisates gave the highest extent of hardening compared to those of HAF black and local clay. Retention in tensile strength of above 90% could be obtained from vulcanisates with three different reinforcing systems.

The investigation on the effectiveness of antioxidants in retaining the tensile strength of ENR-50 after ageing at 125°C was confined to five amine and phenolic antioxidants. The effectiveness of these antioxidants in retaining the tensile strength was deduced as follows: Santoflex 13 > IPPD > Permanax TQ > Permanax WSL > Vulkanox KB. The most effective antioxidant, Santoflex 13, required a low concentration (i.e. 0.2 p.h.r.) in order to give maximum retention in tensile strength and this can be an advantage in terms of reducing compound cost.

Thermal oxidative degradation of an unsaturated rubber generally results in deterioration of its physical properties as well as the service performance properties. Thus, it is desirable to protect the rubber against degradation by using antioxidants or by other means.

The thermal oxidative ageing of ENR has been discussed in various papers[1-4]. Gelling *et al.*[2] believe that the poor ageing of sulphur-cured ENR vulcanisate is attributable to the formation of sulphur acids during the oxidative process. These sulphur acids can catalyse ring-opening of epoxide groups, thus causing crosslinking *via* ether groups. If the extent of crosslinking formed is substantial, the aged vulcanisate can be severely hardened.

It has been demonstrated that a low sulphur vulcanisation system with a high level of sodium carbonate is preferred for improvement in the ageing performance of ENR, in particular ENR-50[4].

This paper is an extension of the work done earlier[4]. In this work, factors other than those discussed in the earlier papers[1-4] were investigated.

EXPERIMENTAL

Materials

Rubbers. ENR-50 prepared from field latex was obtained from the Rubber Research Institute of Malaysia pilot plant using the method of Gelling[5]. The NR used was SMR 5.

Compounding ingredients. The compounding ingredients used were of the recommended grades for rubber. Anhydrous sodium carbonate (98%) was obtained from Fluka AG,

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*Rubber Research Institute of Malaysia, P.O. Box 10150, 50908 Kuala Lumpur, Malaysia

Switzerland. The chemical names of abbreviations used in this paper are given in *Appendix A*.

Procedure

Mixes were prepared on a 30.5 × 15.2 cm two-roll mill. The formulation used in this study is as shown in *Table 1* and the following mixing schedules were adopted:

For HAF Black and Local Clay Mixes

1. Rubber and sodium carbonate

2. Zinc oxide, stearic acid and Permanax TQ

3. Filler and oil

4. Curatives.

For Silica Mixes

1. Rubber, silica, DEG, oil and sodium carbonate

2. Stearic acid and Permanax TQ

3. Zinc oxide

4. Curatives.

Mixing cycle of 20 min was adopted for all the mixes. The mixes were cured to optimum at 150°C. The tensile properties were determined from dumb-bell test pieces cut from the 12.7 × 15.2 × 0.2 cm vulcanised sheets. Vulcanisate properties were tested using the Monsanto Tensometer 500. Accelerated ageing tests were carried on the dumb-bell test-pieces using the Wallace Multicell ageing oven. British Standards *(BS 903 Part A2, 1971* and *BS 903 Part A 19, 1975)* were followed, except the ageing resistance was expressed in terms of per cent retention in the property as shown below:

$$\text{Per cent retention in property} = \frac{\text{Aged value of the property}}{\text{Unaged value of the property}} \times 100$$

RESULTS AND DISCUSSION

Fillers

The results presented in *Figure 1* show the effect of using different types of filler namely HAF black, silica and local clay on the extent

TABLE 1. FORMULATIONS USED IN THE STUDY

Compound	Formulation No.			
	1	2	3	4
ENR-50	100	100	100	100
HAF black (N 330)	40	—	—	40
Silica (VN 3)	—	50	—	—
Local clay	—	—	50	—
Dutrex 737 MB	4	—	—	4
Dutrex 63	—	4	4	—
DEG	—	2.5	—	—
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
Permanax TQ	2	2	2	—
DPG	—	0.5	0.5	—
MOR	1.5	1.5	1.5	3.0
PVI	0.3	—	—	0.3
Sulphur	Variable	Variable	Variable	0.5
Sodium carbonate	Variable	Variable	Variable	3.0
Antioxidant	—	—	—	Variable

of hardening (as shown by the increase in per cent retention in modulus at 100% strain, M100) of ENR-50 vulcanisates after being subjected to three days ageing at 100°C. As illustrated by the results, the silica-filled ENR-50 vulcanisates gave the highest extent of

hardening compared to those of HAF black and local clay.

The degree of hardening shown by the three types of fillers differentiates the ability of each filler to promote crosslinking during the ageing
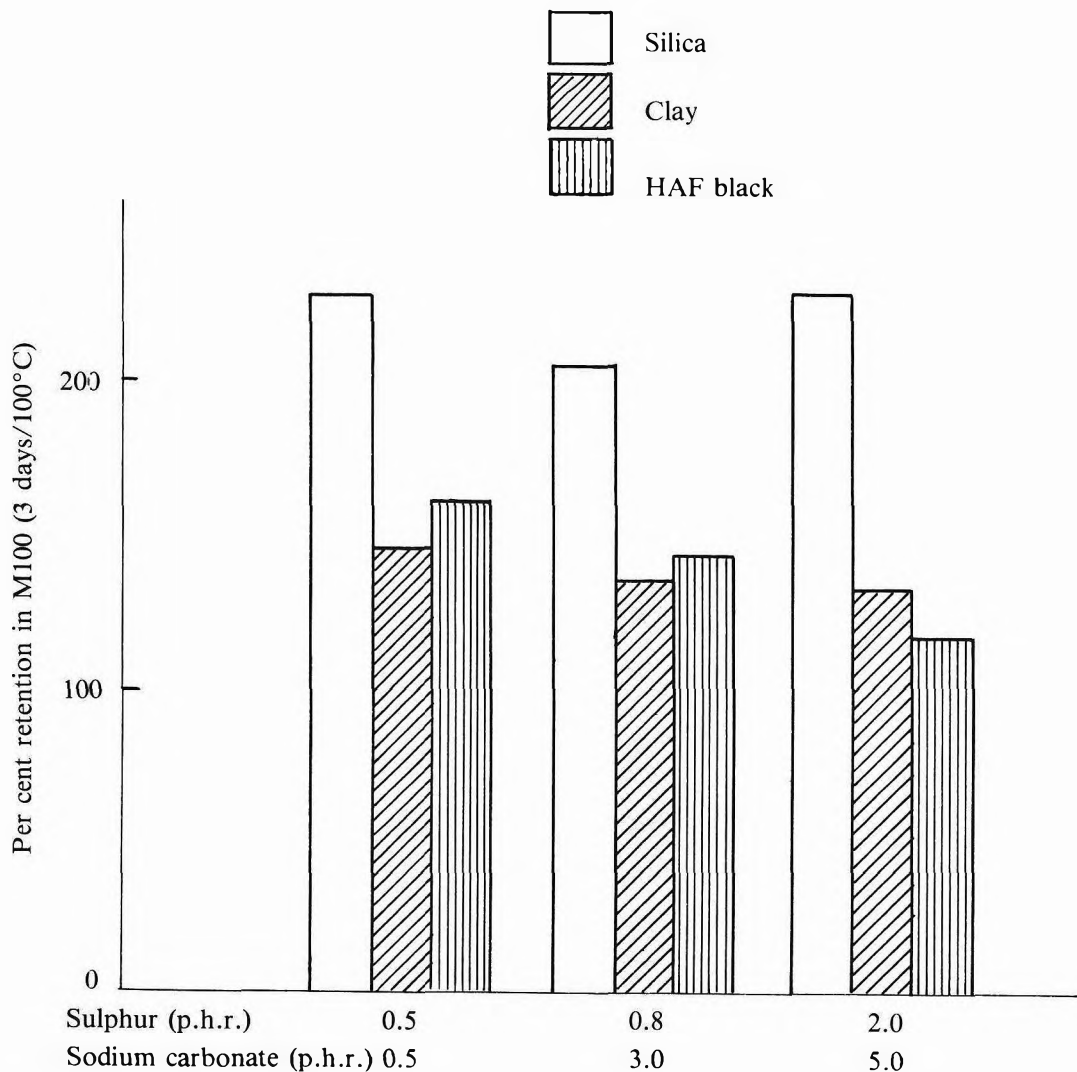

Figure 1. Per cent retention in M100 (3 days/100°C)

process. The enhancement of the formation of crosslinks shown by silica is also reflected by the earlier observation[6] whereby silica gave good reinforcement to ENR-50 without the use of coupling agents. The increased hardening during ageing of ENR-50 silica-filled vulcani-

sates could be due to ENR-50/silica reaction during ageing.

As shown in *Figures 2-4*, the silica-filled ENR-50 vulcanisate gave the highest extent of hardening. This increase in crosslink density
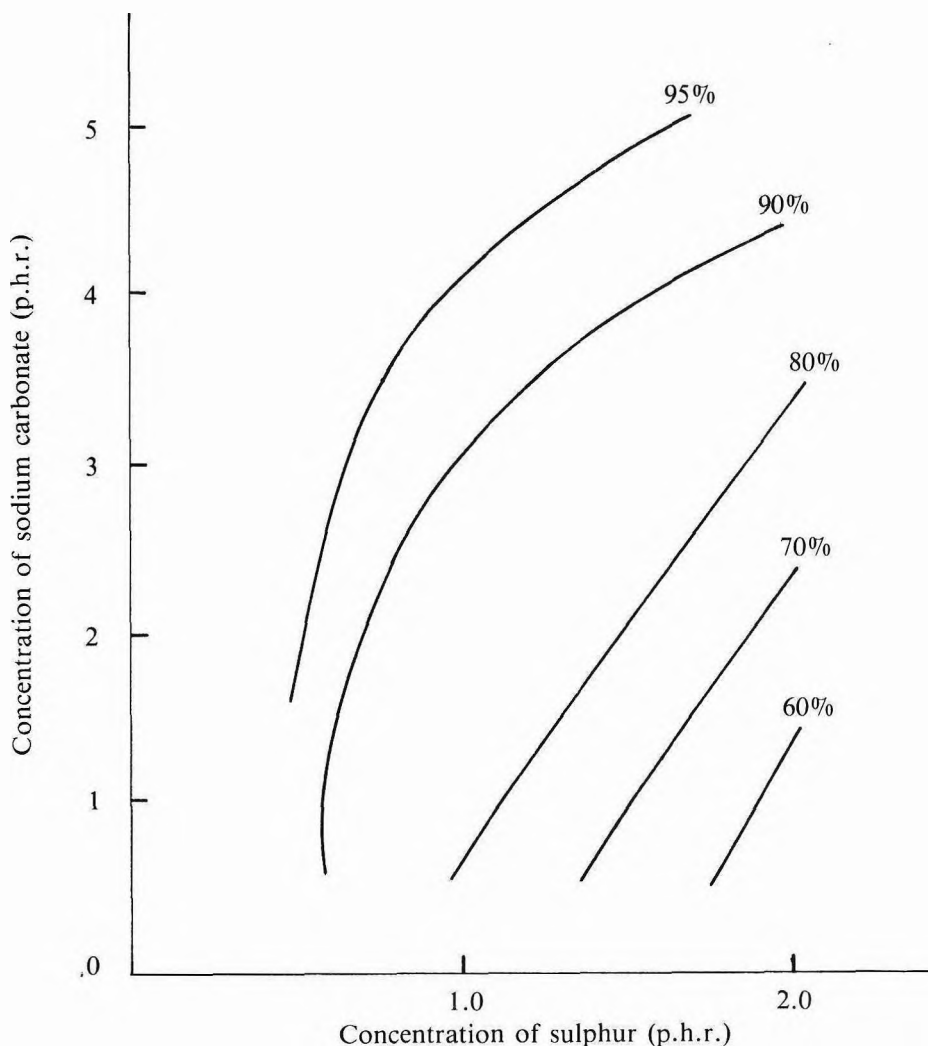

Figure 2. Effect of concentrations of sulphur and sodium carbonate on per cent retention in tensile strength (3 days/100°C) — silica-filled ENR-50.
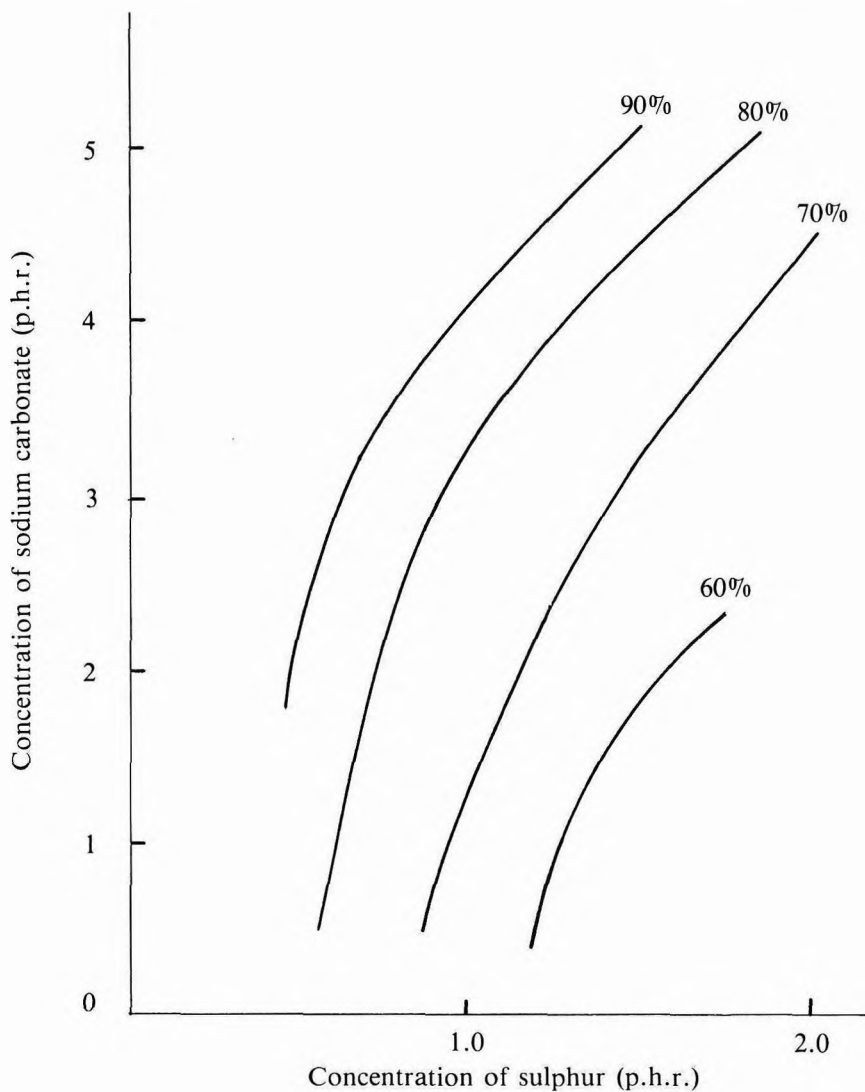
Figure 3. Effect of concentrations of sulphur and sodium carbonate on per cent retention in tensile strength (3 days/100°C) — clay-filled ENR-50.

was not substantial enough to result in a decrease in tensile strength as shown in *Figure 2*. However, the increase in the crosslink density was sufficient to result in lower elongation at break as shown in *Figure 5*. For both HAF black and clay-filled vulcanisates, retention in elongation at break of above 80% could be obtained by using formulations with appro-

priate levels of sodium carbonate and sulphur as shown in *Figures 6* and *7*.

Level of Unsaturation

During the ageing of NR and ENR vulcanisates at 125°C, a severe softening effect of either NR[7,8] or ENR-25[4] vulcanisate could
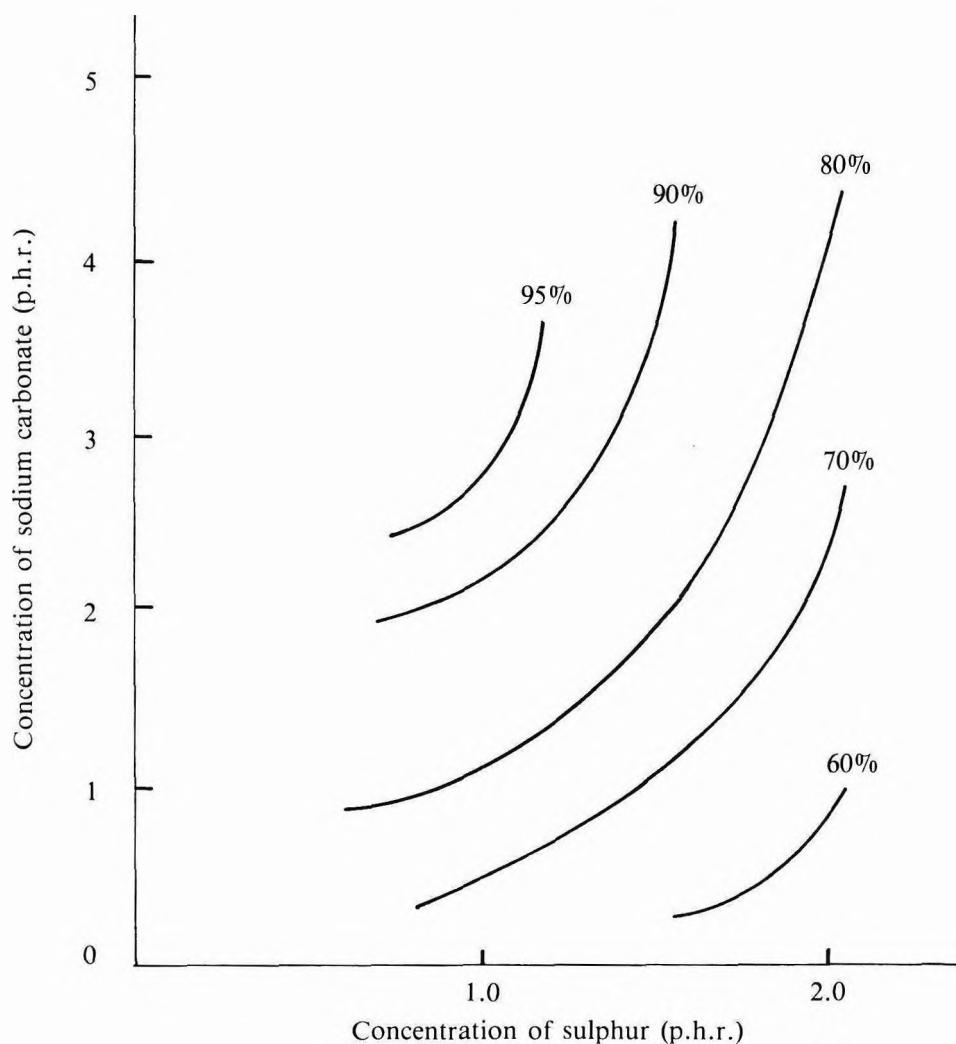
Figure 4. Effect of concentrations of sulphur and sodium carbonate on per cent retention in tensile strength (3 days/100°C) — HAF black-filled ENR-50.

occur while in the case of ENR-50[3], hardening of the vulcanisate was observed. This softening effect is presumably due to main-chain scissions occurring at exceptionally high temperature. Since both NR and ENR-25 contain a higher level of unsaturation compared to ENR-50, a higher extent of main-chain scissions would be expected for both NR and ENR-25. However, if the ageing of either NR[7,8] or ENR-25[1] is carried out at 100°C, the main-chain scissions occurring are presumably not substantial and thus improvement in the ageing performance of those rubbers can be obtained by the use of an efficient vulcanisation (EV) system with antioxidants for NR or EV system with bases and antioxidants for ENR-25.

Figure 5. Effect of concentrations of sulphur and sodium carbonate on per cent retention in elongation at break (3 days/100°C) — silica-filled ENR-50.

Antioxidants

Antioxidants are known to inhibit main-chain scissions occurring during the ageing of NR. Thus it would be interesting to observe the effect of various antioxidants in minimising the main-chain scissions occurring in ENR, in particular ENR-50.

The results shown in *Figure 8* illustrate the effect of some commercially available antioxidants on the per cent retention in M100 of ENR-50 vulcanisates based on a EV system with 3 p.h.r. of sodium carbonate. The results shown in *Figures 8–10* were based on *Formulation 4* of *Table 1*. As shown in *Figure 8,* the per cent retention in M100 of the vulcani-
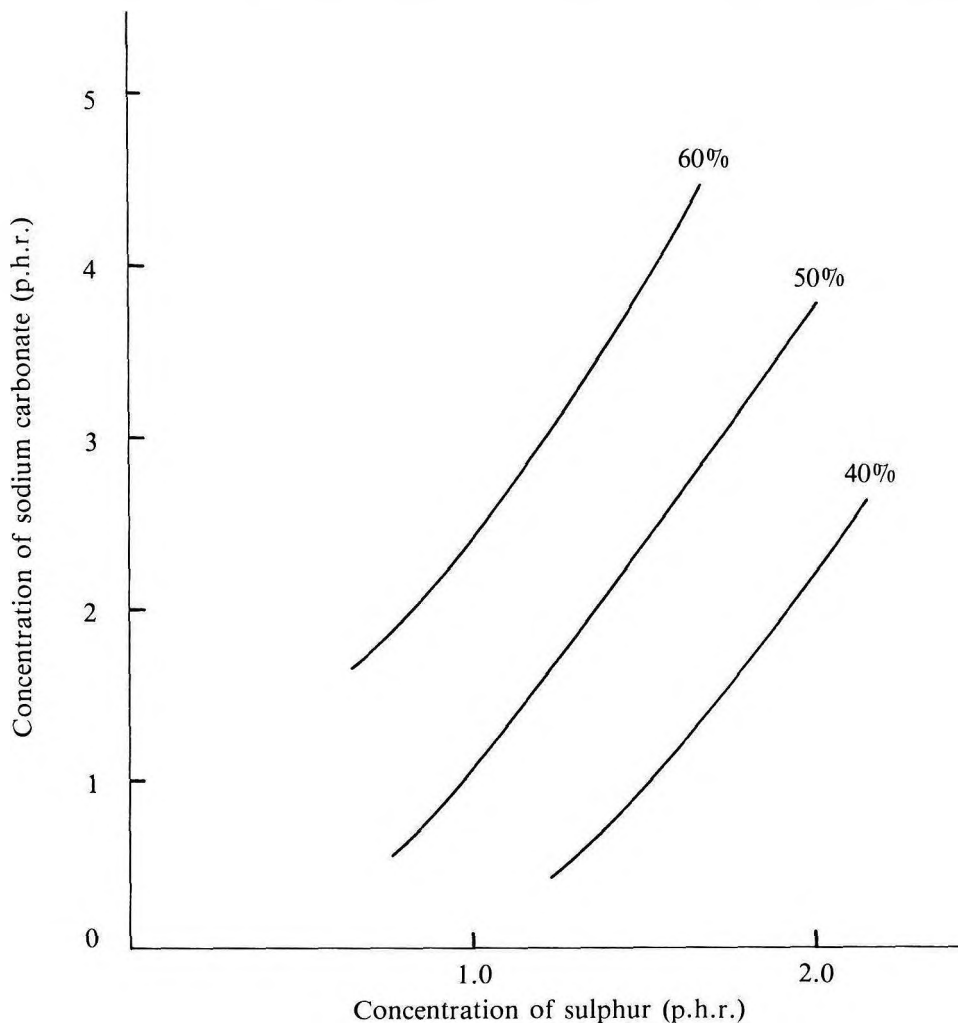
Figure 6. Effect of concentrations of sulphur and sodium carbonate on per cent retention in elongation at break (3 days/100°C) — clay-filled ENR-50.

sate depends on the concentrations and the types of the antioxidant. In the absence of any antioxidant, the retention in M100 was 89%, and this is presumably due to the predominant effect of the main-chain scissions as discussed earlier. The per cent retention in M100 of the vulcanisate increased with increasing concentration of antioxidant. Amine-type antioxidants

(*i.e.* Santoflex 13, IPPD and Permanax TQ) were found to be more effective compared to the phenolic type antioxidants in inhibiting the softening of the vulcanisate.

In the ageing process of ENR-50 black-filled vulcanisate based on the EV system, two main reactions are presumably taking place: cross-
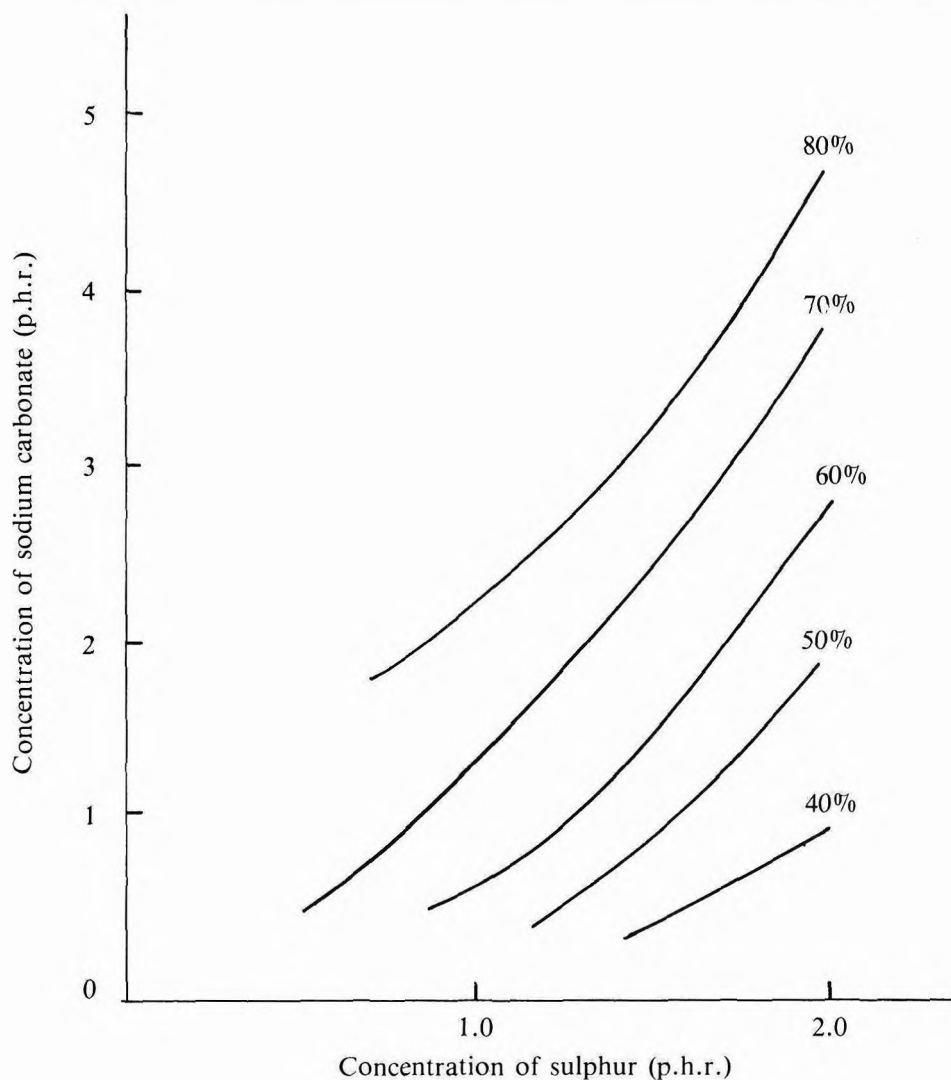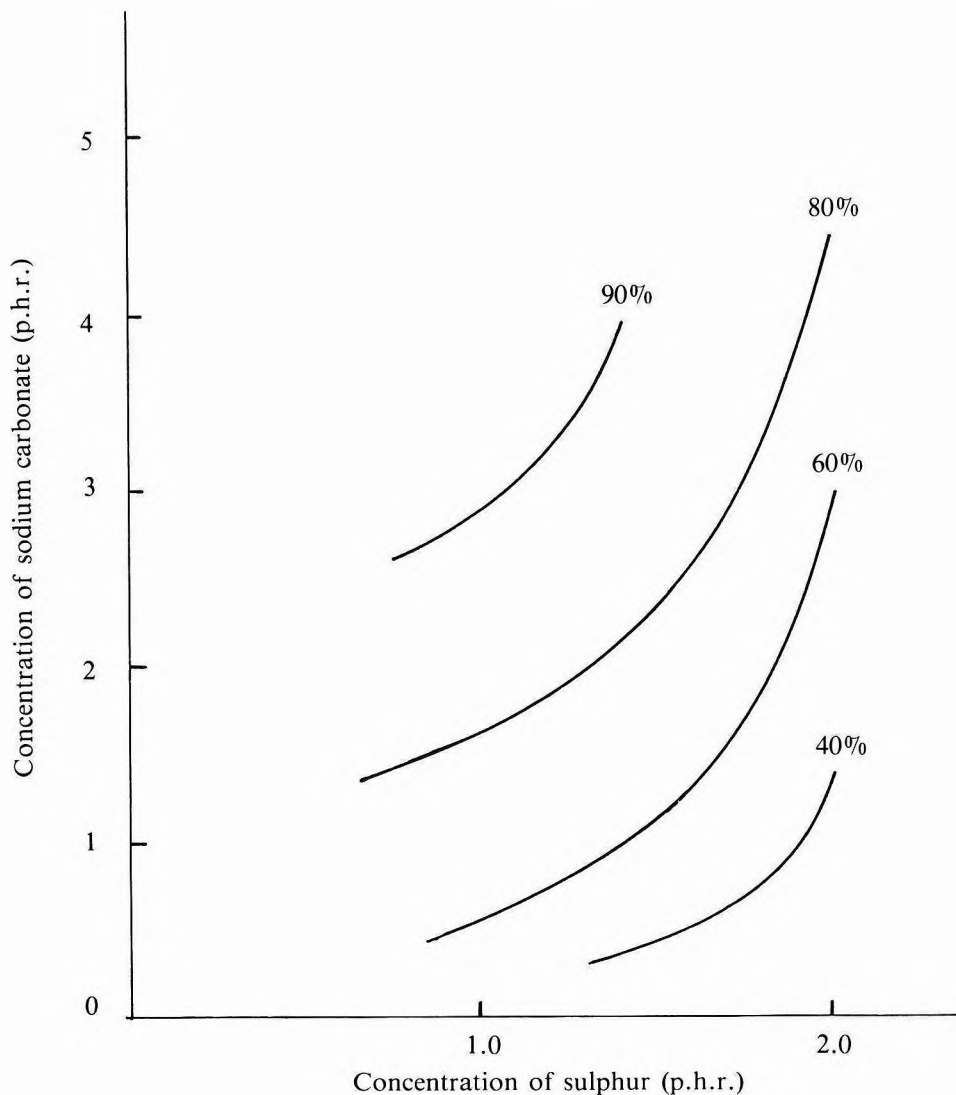
Figure 7. Effect of concentrations of sulphur and sodium carbonate on per cent retention in elongation at break (3 days/100°C) — HAF black-filled ENR-50.

linking reactions due to the presence of acid and the main-chain scissions. The degree of crosslinking could be controlled by the levels of the base, sulphur and accelerator added while the extent of the main-chain scissions could be minimised by the level and the type of antioxidant present. Thus the net effect of these two reactions will eventually determine

the modulus of the aged vulcanisate, and consequently the tensile strength and the elongation at break of the vulcanisate.

The effectiveness of the various investigated antioxidants in retaining the tensile strength after ageing can be deduced as follows: Santoflex 13 > IPPD > Permanax TQ > Permanax
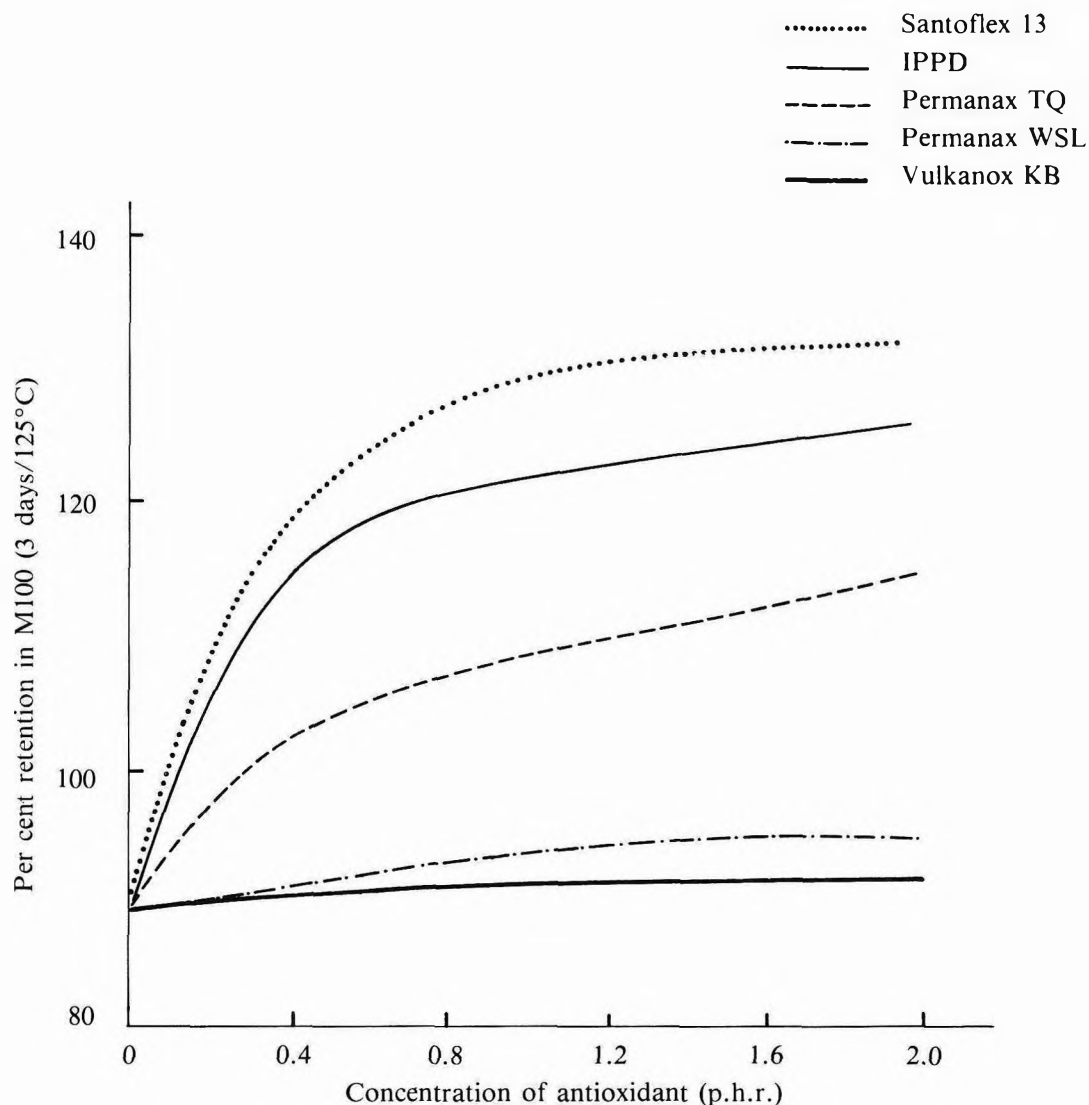
Figure 8. Effect of antioxidants on per cent retention in M100 (S/MOR/sodium carbonate: 0.5/3.0/3.0).

WSL > Vulkanox KB. For the most effective antioxidant (Santoflex 13) the maximum per cent retention in tensile strength could be obtained at a low concentration of the antioxidant (*i.e.* 0.2 p.h.r.) This can be an advantage in terms of reducing the compound cost.

The effect of types and concentrations of the antioxidants on the retention in elongation at break is shown in *Figure 10*. Both amine-type antioxidants (*i.e.* Santoflex 13 and IPPD) gave significant decrease in aged elongation at break at high concentrations of the antioxidants.
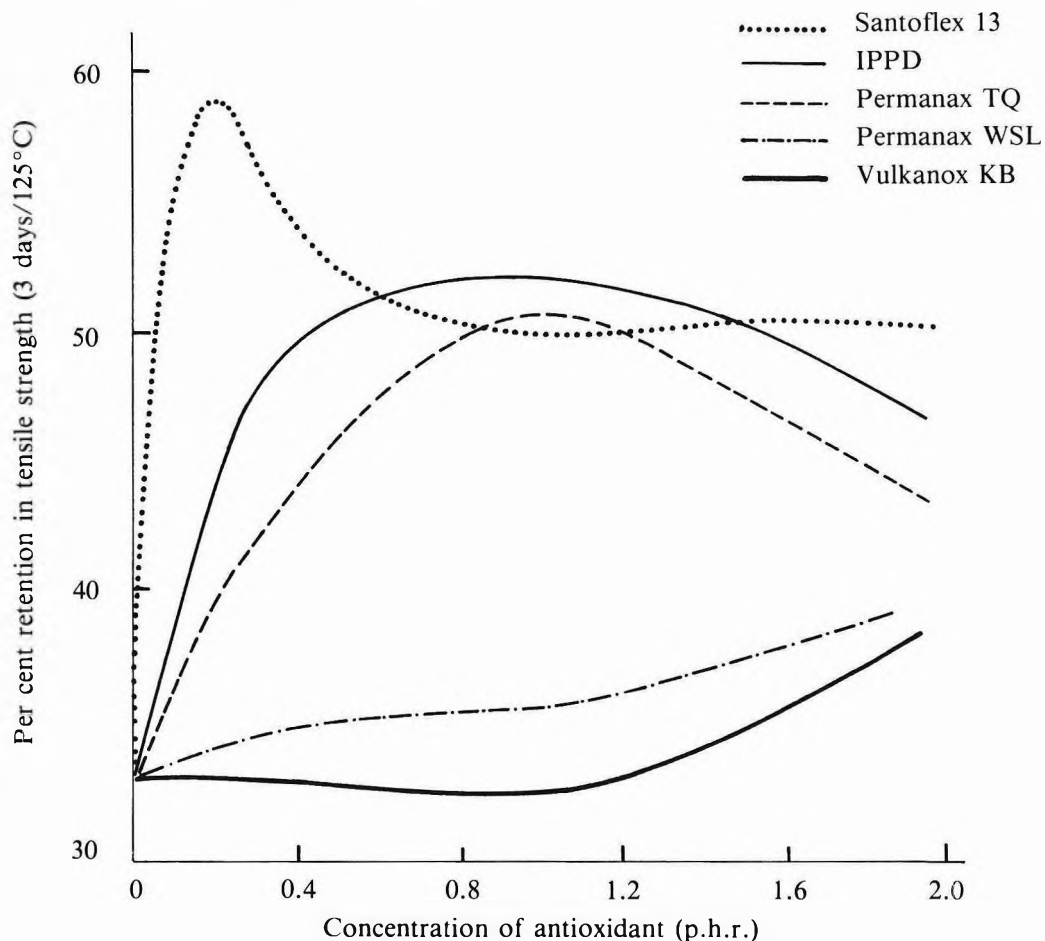
Figure 9. Effect of antioxidants on per cent retention in tensile strength (S/MOR/sodium carbonate: 0.5/3.0/3.0).

The mechanism developed by Bolland[9] to account for amine and phenolic antioxidant activity is illustrated in *Figure 11*. Reactions involving *Steps 3* and *6* are the most important for antioxidant action and these reactions remove the free radical functionality from the rubber so that normal oxidative degradation of the rubber is halted. The differences in the activities of the amine and phenolic antioxidants in these reactions explain the results observed earlier, *i.e.* the amine antioxidants were more effective than the phenolic antioxidants. If reactions involving *Steps 2* and *4* become important, enhanced oxidative degradation of the rubber can occur. Thus, it is important that the level of antioxidant be kept at the optimum since excess antioxidant can result in a pro-oxidant effect[10]. As shown in the earlier results, the optimum level required in retaining tensile strength after ageing with Santoflex 13, IPPD and Permanax TQ were found to be 0.2, 0.8 and 1.0 p.h.r. respectively.
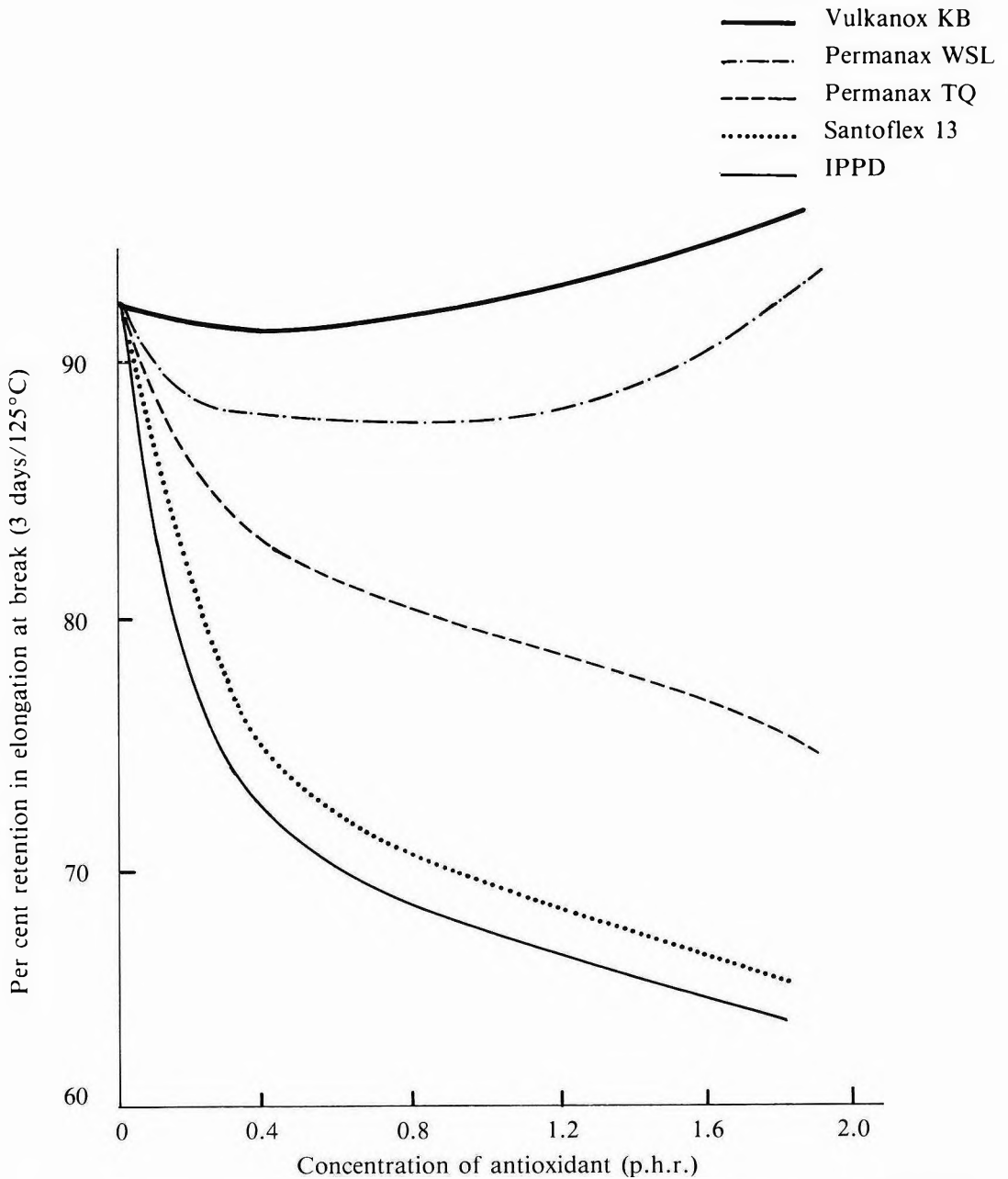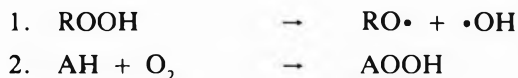
Figure 10. Effect of antioxidants on per cent retention in elongation at break (S/MOR/ sodium carbonate: 0.5/3.0/3.0.

It is also possible that the main-chain scissions or softening effect are minimised at higher levels of antioxidant and consequently the tensile strength which depends on the net result of both softening and hardening effects is affected by the level of antioxidant added.

Initiation

1. ROOH $\longrightarrow$ RO$\cdot$ + $\cdot$OH

2. AH + O$_2$ $\longrightarrow$ AOOH

Transfer

3. RO$\cdot$ / RO$_2\cdot$ + $\longrightarrow$ ROH / ROOH + A$\cdot$

4. A$\cdot$ + RH $\longrightarrow$ AH + R$\cdot$

Termination

5. 2 ROO$\cdot$ $\longrightarrow$)

6. 2 A$\cdot$ $\longrightarrow$) Stable products
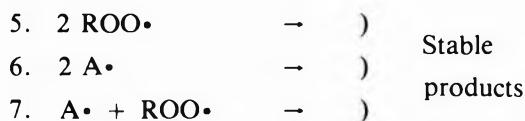
7. A$\cdot$ + ROO$\cdot$ $\longrightarrow$)

Figure 11. Mechanism of amine and phenolic antioxidant activity (AH refers to the antioxidant).

CONCLUSIONS

Apart from the factors which have been discussed in the previous papers, this study showed that both fillers and antioxidants influenced the ageing performance of ENR-50 vulcanisates. Of the three fillers investigated, silica gave the highest extent of hardening to ENR-50 on ageing. In the case of antioxidants, their concentrations and types were found to be critical in determining the tensile properties of the aged ENR-50 vulcanisates.

ACKNOWLEDGEMENT

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DEG	Diethylene glycol
DPG	Diphenylguanidine
MOR	N-oxydiethylene benzothiazole-2-sulphenamide
PVI	N-(cyclohexylthio)pththalimide
IPPD	N-isopropyl-N'-phenyl-*p*-phenylenediamine
Santoflex 13	N-(1,3-dimethylbutyl)-N'-phenyl-*p*-phenylenediamine
Permanax TQ	Poly-(2,2,4-trimethyl-1,2-dihydroquinoline)
Permanax WSL	Methylcyclohexylxylenol
Vulkanox KB	2,6-Di-(tert-butyl)-*p*-cresol
Dutrex 737 MB	Aromatic processing oil
Dutrex 63	Naphthenic processing oil

Natural Rubber Truck Tyre Compounds for Improved Wear Performance

C.S.L. BAKER* AND I.R. WALLACE*

The trend to pre-cure treads has reduced the need to use NR in heavy-duty truck tyre retreading. Thus, NR compounds have had to compete solely on a tread life basis where, under normal highway conditions with relatively low severity, SBR/BR compounds would probably be found superior owing to the reversion characteristics of NR. A high stearic acid semi-EV system has been developed for NR, whose abrasion resistance does not, as is usually observed, deteriorate on overcure. In fleet trials, 80/20 NR/BR treads based on this formulation were found to come close to a high mileage SBR/BR tread under low severity conditions, and surpass it under high severity conditions. Rig testing has also shown the new NR compound to have improved rolling resistance and lower running temperatures. In a second series of trials, NR dominant compounds with this new curing system and an increased proportion of BR were examined, and a formulation has been found which has a longer tread life than the synthetic control under low severity conditions.

Modern heavy-duty truck tyres of radial construction generally contain in excess of 80% natural rubber (NR) on their overall polymer content. The reason for this is the virtually essential need of NR's high green strength and tack to build such tyres. For many years, NR was also dominant in their retreading providing excellent tack onto the buffed carcass and low heat generation in the high shoulder regions. However, in recent years, precure retreading methods have been developed which no longer require tack in the tread itself during the building process, nor particularly low heat generation in the final compound since the shoulder regions of these treads are substantially thinner.

As a result, the majority of precure tread formulations are based on SBR or SBR/BR blends as those have been found to exhibit excellent wear performance under low severity (highway) conditions. Indeed, it is well known that a normal NR compound is likely to undergo reversion during its long service life which will, as has been demonstrated in the laboratory, adversely affect abrasion resistance. It is not altogether surprising therefore that NR has become a less favoured polymer for precure

treads of heavy-duty truck tyres to be used under normal highway conditions. For high severity (on-and-off the road) and many drive axle applications, however, where a premium tread is required, then NR is preferred since it has significantly better resistance to chipping, chunking and tearing, and there is evidence to suggest that these properties might even be improved by reversion[1].

The object of this work therefore is to develop new NR-rich truck tyre compounds which are capable of out-performing the existing synthetic rubber formulations under both high and low severity wear conditions. This paper outlines the laboratory results which indicated the compounds most suitable for fleet trials carried out on 1100×22.5 tyres by a UK long distance haulier. It demonstrates in the first series of trials conducted in 1983/84 how a reversion resistant high stearic acid semi-EV system based on an 80/20 NR/BR compound gives significantly better wear than a normal stearic acid semi-EV system under low severity conditions, and how even further improvements have been achieved in a second series of trials in 1985/86 with the same cure system and an increased BR content. The additional

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*Malaysian Rubber Producers' Research Association, Brickendonbury, Hertford, SG13 8NL, United Kingdom

benefits of the use of NR to provide lower rolling resistance, and less heat generation in the tyre, are also discussed.

<div align="center">EXPERIMENTAL</div>

Mixing

Since our Research Institute does not possess a full-size internal mixer, the compounds for heavy-duty truck tyre retreading were mixed outside by Avon Tyres Ltd. according to our instructions in a No. 11 Banbury.

Four stages were used for the NR compounds at 40 r.p.m. as follows:

1. A 4.0 min mastication to achieve a Mooney (ML 1 + 4) at 100°C of 58 – 60

2. A masterbatch incorporating BR, black, oil, antidegradant, zinc oxide and stearic acid for 3.0 min

3. A re-mix stage of 2.0 min 15 s

4. A final pass of 2.0 min 10 s during which the sulphur and accelerator were added.

In the case of the synthetic rubber compound, a three-stage mix was used as follows:

1. A masterbatch stage at 60 r.p.m. incorporating black, oil, antidegradant, zinc oxide and stearic acid for 2.0 min 15 s.

2. A re-mix stage at 40 r.p.m. for 2.0 min 15 s.

3. A final pass of 2.0 min 10 s during which the sulphur and accelerator were added.

Retreading

The retreading of 1100 × 22.5 radial truck tyres used for the service trials was also conducted outside by the Vacu-Lug Traction Tyre Company. First life casings of 16-ply construction were selected for use from one original manufacturer. They were buffed to the same template contour and treated with a light spray application of vulcanisable tyre cement. The new treads were applied with a Barwell Pressure Builder and new sidewalls applied in a manual operation. All tyres were vulcanised for 90 min at 150°C in Michelin ZZ design matrices with a 13 mm skid depth. The heat source was from the matrix side only.

Service Trials

In the fleet trials, the retreaded tyres were fitted to the dual drive axles of rigid Foden eight wheel tipper trucks with a 30-tonne carrying capacity, the axle arrangement of which is shown in *Figure 1*. The vehicles were used primarily for long hauls on main highways and minor roads. Tread depth measurements were made using a Vernier depth gauge in the inner, two centre and outer grooves. Two sets of readings were taken at each time of measurement on opposite sides of the tyre, and all eight values recorded.

The first series of service trials were conducted in the UK between September 1983 and June 1984. From November to mid-May cool conditions generally existed while the periods of September, October and June were relatively dry and warm.

The second series of trials were commenced in June 1985 and results completed in September 1986. Until November 1985 conditions were generally dry and warm, while November to April were cooler than normal UK winter and spring conditions, followed by a warm wet summer.

Rolling Resistance and Heat Generation

Both these tests were conducted on a Heenan-Froude tyre test rig with a 1.71 m diameter wheel. The tyres used for these tests were carefully selected to ensure equivalent carcass and tread weights to within ± 250 g.

Rolling resistance was measured from the power consumption of the rig with the tyres under 80% of their rated load less the power to run the rig with the same tyres under skim contact. The initial cold inflation pressure was set at 724 kPa and was not regulated during the test. The tyres were run to equilibrium temperature for each speed increment of 30, 65 and 100 km per hour.
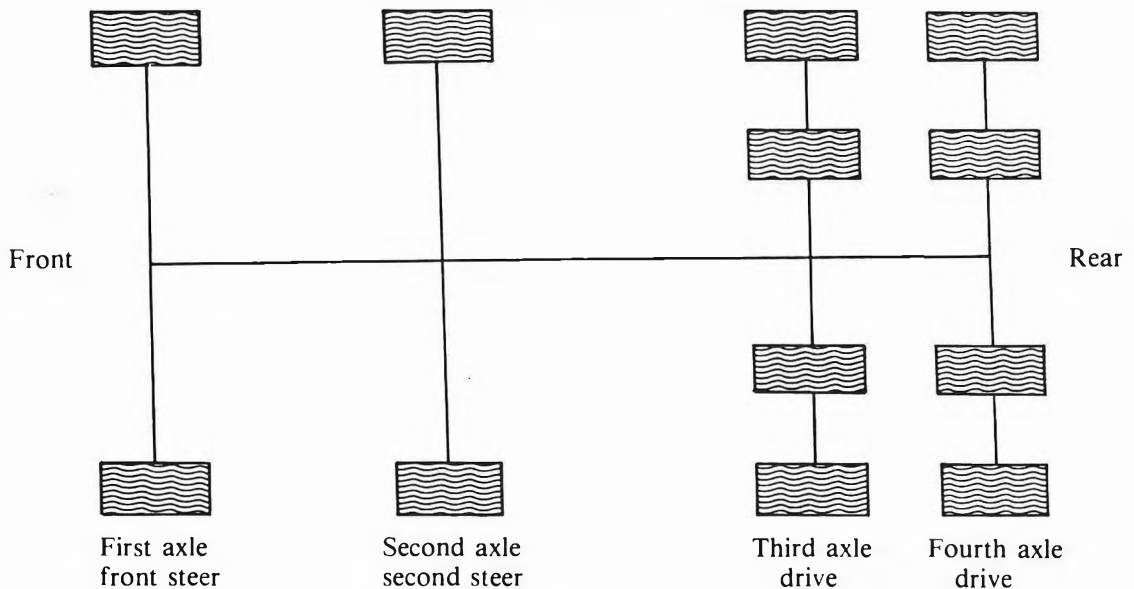
Front   Rear

First axle   Second axle   Third axle   Fourth axle
front steer   second steer   drive   drive

Figure 1. Truck axle arrangement of rigid eight-wheel drive tipper trucks.

The same load, inflation pressure and speeds were used in the heat generation studies. The temperatures were measured by means of a pyrometer needle probe inserted into the shoulder of the tread and at the base of the undertread in the central grooves at six pre-determined points. The insertion depth into the shoulder was 20 mm from the side of the tyre.

Laboratory Measurements

Physical testing procedures were as those normally used at MRPRA[2] as follows:

Tensile strength to *ISO 37*

Hardness to *ISO 48*

Resilience, Dunlop Tripsometer, to *BS 903 Part A8*

Tear strength, trouser, to *ISO 34*

Heat build-up, Goodrich Flexometer, to *ISO 4666/3*

Abrasion, DIN to *ISO 4649* — in course of preparation

Abrasion, Akron, to *BS 903, Part A9, Method C.*

RESULTS AND DISCUSSION

Laboratory Data

It is a well known fact that although natural rubber exhibits excellent initial physical properties in terms of strength, resilience, heat build-up, *etc.*, it is at a disadvantage in its reversion characteristics compared to synthetic rubbers such as SBR. It has already been explained that NR is dominant in new heavy-duty truck tyres on account of its overwhelming advantage in maintaining green-tyre uniformity. However, for retreading its reversion characteristics generally put it at a disadvantage. There are two, possibly mythical reasons for this:

● During the retreading process, as distinct from the cure cycle of the original tyre, heat is provided solely from the outside of the tyre, such that for the base of the tread to be fully cured the surface has necessarily been considerably over-cured.

● During the service life of the tyre, there will be occasions of high ambient temperatures combined with heavy loads

and high speeds when the running temperature of the tyre will come close to that of its original vulcanisation temperature, and again reversion will occur.

With the known loss of laboratory abrasion resistance that occurs on reversion, it is not altogether surprising that the retread industry is concerned over loss of mileage which might occur if NR-rich compounds are used. It is with this aspect in mind that new curing systems are being sought which exhibit improved reversion resistance and, more important still, show a high retention of abrasion resistance on overcure. One such system is a high stearic acid semi-EV system shown in *Table 1*. Here the Monsanto Rheometer data has been used to indicate the reversion resistance of four different compounds as an initial screening exercise. Three NR-rich, 80/20 blends cured with three different vulcanising systems have been com-

pared to a typical SBR/BR truck tread compound, and their relative reversion resistance estimated by the time taken at 150°C to reach 5% reversion. As might be expected, a conventional high sulphur/low accelerator cure system reverts rapidly at 150°C, while a 50% improvement is shown by a semi-efficient system based on 1.2 parts sulphur/1.2 parts accelerator and the normal 2 parts stearic acid. However, it has been found that if that stearic acid concentration is increased to 6 parts, then the reversion resistance is improved by a factor of two over the semi-EV with 2 parts stearic acid, which is then greater than that of the SBR/BR reference compound evaluated.

Such an observed increase in resistance to reversion does not necessarily mean that abrasion is unaffected by overcure, and therefore this feature was examined as a next step and shown in *Table 2*. Here the same four compounds were vulcanised to 90% of

TABLE 1. TREAD COMPOUNDS FOR HEAVY-DUTY TRUCK TYRES (FIRST STUDY)

Item	NR/BR (80/20)			SBR/BR
	Conventional system	Normal stearic semi-EV	High stearic semi-EV	Reference compound
Tread compounds				
SMR 20	80	80	80	
Med *cis* 1,4 BR	20	20	20	45
SBR 1712				37
SBR 1500				27
N 375 black	55	55	55	60
High aromatic oil	8	8	8	5
Zinc oxide	4	4	4	4
Stearic acid	2	2	6	2
Antidegradant[a]	2	2	2	2
Sulphur	2.3	1.2	1.2	2.0
MBS[b]	0.6	1.2	1.2	1.2
Monsanto rheometer (150°C, 1° arc, 50 range)				
t_{max} (min)	24	20	39	44
$t_{5\%R}$ (min)	43	65	138	120

[a]N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine

[b]N'-oxydiethylene benzothiazole-2-sulphenamide

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TABLE 2. EFFECT OF OVERCURE ON LABORATORY ABRASION OF TRUCK TREAD COMPOUNDS

Laboratory abrasion	NR/BR (80/20)			SBR/BR
	Conventional system	Normal stearic semi-EV	High stearic semi-EV	Reference compound
DIN abrasion				
(Relative wear indices)				
Cured 90% optimum	110	110	110	140
Plus 70 min/150°C	86	85	106	131
Retention (%)	78	85	96	94
Akron abrasion				
(mm^3/500 revolutions)				
Cured 90% optimum	12.7	13.9	12.3	11.2
Plus 70 min/150°C	19.5	22.6	15.5	13.0

optimum cure and to 70 min overcure at 150°C. Both laboratory DIN and Akron abrasion measurements confirmed that the high stearic acid semi-EV system in an 80/20 NR/BR blend showed only a minimal reduction in abrasion resistance on overcure. DIN abrasion was only 4% lower as a result of the extra 70 min at 150°C compared to a 15% loss with the same cure system and 2 parts stearic acid, and a 22% loss with the conventional cure. Similarly with Akron abrasion, the conventional and semi-EV cures with normal stearic acid showed 7–8 mm^3 per 500 revolutions increase in abrasion loss on the 70 min overcure compared to only 3 mm^3 or 2 mm^3 per 500 revolutions for the high stearic acid NR compound and the synthetic control. The high stearic acid semi-EV 80/20 NR/BR compound therefore appears to have substantial promise for truck tyre retreading, with retention of abrasion properties on overcure similar to the synthetic reference compound, although it must be noted that the latter has an overall higher abrasion index on account of its 45 parts BR content.

It is also important that it is not only the abrasion properties of the high stearic acid NR compound which are retained on overcure. As *Table 3* indicates, benefits over the other NR formulations are also found in the retention of modulus, tensile strength, elongation at break and hardness. These in themselves should enhance tyre tread performance, but more important are the tear, resilience and heat build-up properties in the second half of *Table 3*. Although tear strength of the high stearic acid semi-EV is not as high as that with the normal stearic acid concentration, it is above that of the conventional cure and significantly above that of the synthetic reference compound accompanied by a greater retention on overcure. Similarly in resilience, the high stearic acid semi-EV has a resilience above that of its normal stearic equivalent, but below that of the conventional cure. However, it exhibits a 93% retention on overcure giving it the highest resilience of all four compounds studied. This would be a contributory factor to the remarkably low Goodrich heat build-up values exhibited by the high stearic acid compound. This low extent of heat generation reflects more than the simple differences in resilience, and one possible explanation might be internal lubrication effects of the increased fatty acid/stearate complex, or possibly differing dynamic modulus. Whatever the cause, the laboratory heat build-up test indicates that the high stearic acid semi-EV compound will be cooler running than any of the other compounds under study. This, therefore, along with its retention of abrasion resistance on overcure, made it essential that this high stearic acid formulation be evaluated as actual retreads in service trials.

TABLE 3. EFFECT OF OVERCURE ON PHYSICAL PROPERTIES OF TRUCK TREAD COMPOUNDS

Physical property	NR/BR (80/20)			SBR/BR
	Conventional system	Normal stearic semi-EV	High stearic semi-EV	Reference compound
Initial M300 (MPa)	13.5	10.6	11.4	13.2
70 min/150°C overcure (% retention)	68	81	93	98
Initial tensile strength (MPa)	24.0	22.3	22.6	20.1
70 min/150°C overcure (% retention)	69	86	91	96
Initial elongation at break (%)	475	560	510	390
70 min/150°C overcure (% retention)	94	97	99	110
Initial hardness (IRHD)	66	67	66	68
70 min/150°C overcure (% retention)	91	93	98	100
Initial tear, trouser (kN/m)	20.2	35.3	24.6	14.4
70 min/150°C overcure (% retention)	62	94	83	77
Initial resilience, Dunlop (%)	61	55	58	54
70 min/150°C overcure (% retention)	80	93	93	91
Initial HBU, Goodrich (T°C)	93	94	69	99
70 min/150°C overcure (T°C)	104	96	74	101

FLEET TESTING RESULTS

First Service Trials

Following the outcome of the laboratory testing of the high stearic acid semi-EV 80/20 NR/BR compound, forty-eight 1100 × 22.5 heavy-duty radial truck tyres were retreaded with three of the four compounds shown in *Table 1*. Those chosen were the two NR/BR blends with semi-EV cure systems to directly establish the effect of the high stearic acid concentration, and the SBR/BR compound to compare the wear performance of the NR-rich treads to that of a typically used synthetic formulation. The use of six eight-wheel drive vehicles as shown in *Figure 2* permitted the allocation of eight tyres per compound to be fitted to both the third (forward) drive axles and the fourth (trailing) drive axles. The actual distribution of these tyres is indicated in *Figure 3* demonstrating the comprehensive

fitting arrangements used. Before discussing the results of these trials, it must be noted that the abrasion conditions of the third and fourth drive axles are by no means the same. The tyres on the fourth drive axles are subjected to higher severity than those on the third axles owing to the effects of higher cornering forces and load transfer more prevalent on the tail end of the vehicles. The greater degree of slip on cornering consequently leads to a higher extent of transverse wear. The trials therefore enabled testing of the tyres under both high severity and low severity wear conditions at the same time.

Figure 4 shows the wear performance of the three compounds, and the radical difference in tread life between the two sets of drive axles is immediately obvious. The figures represent an average predicted mileage from the eight tyres tested in each position. Under low severity conditions (third axles), which is where SBR/BR synthetic formulations are known to exhibit

Figure 2. Dual drive Foden eight-wheel tipper truck.

high mileage, the 80/20 NR/BR compound with a normal stearic acid semi-EV cure system only achieved 72 000 km compared to 113 000 km by the synthetic compound. This indeed confirmed that such NR-rich formulations are inferior under low severity conditions. However, the new high stearic acid semi-EV formulation with 80/20 NR/BR lasted 103 000 km — a very significant improvement in wear performance compared to that with the normal stearic acid concentration, and indeed was within 10% of the synthetic SBR/BR tread life. Under high severity conditions (fourth axles) on the other hand, the positions are totally reversed. Here the synthetic compound only achieved 46 000 km compared to the normal stearic acid

semi-EV 80/20 NR/BR compound which lasted 64 000 km. The new high stearic acid formulation fell between the two at 53 000 km. The results of this first series of trials[3], conducted in 1984, thus indicated that an NR-rich compound cured with a reversion resistant high stearic acid semi-EV system could give wear performance much closer to that of a typical synthetic tread under low severity conditions, while still exceeding the latter under high severity conditions. The next stage would be to optimise the NR/BR ratio to provide a compound capable of exhibiting superior wear performance under both severity conditions compared to the synthetic compound, which it must be noted contained 45 parts BR, known
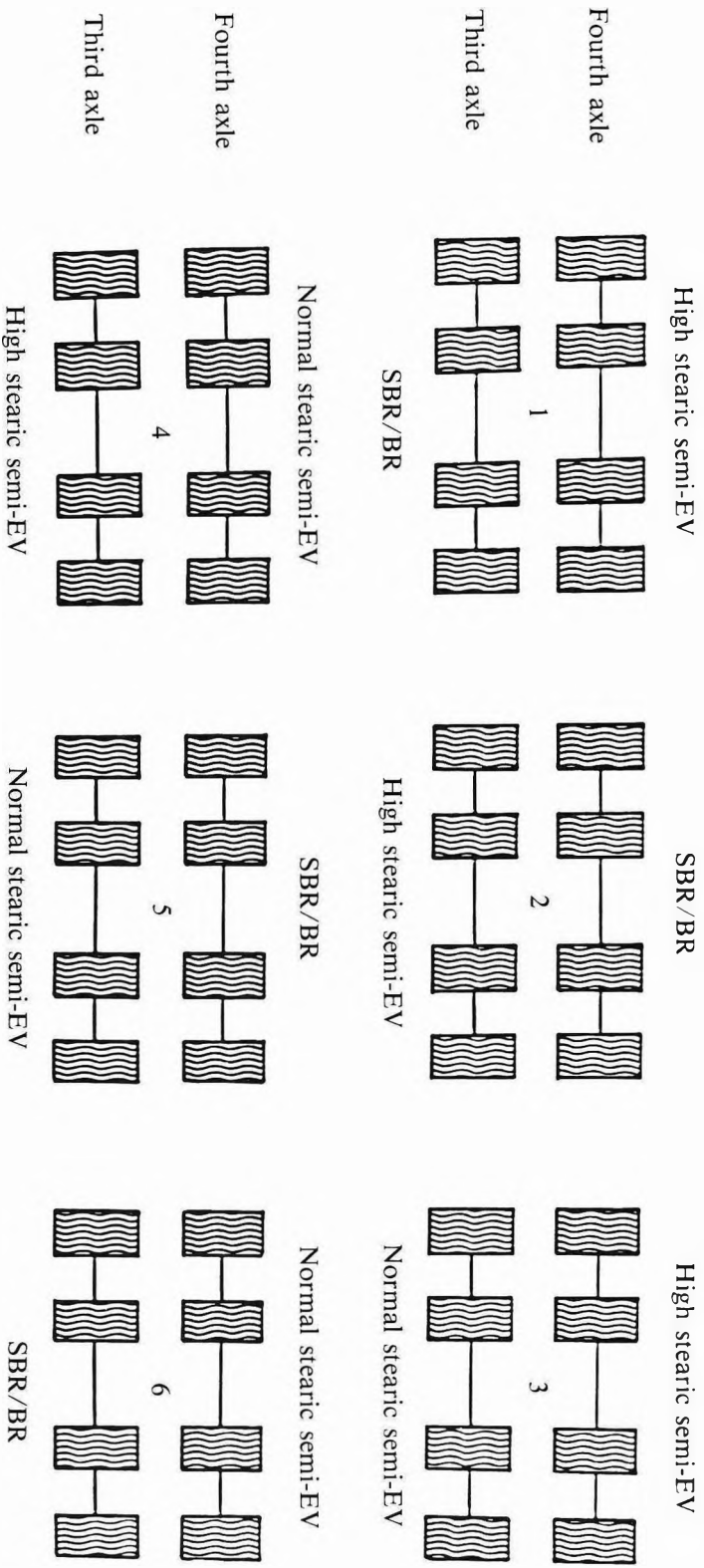
Figure 3. Heavy-duty truck tyre retread fitting arrangement (first service trial).

Wear performance ('000 km)

Low severity – 3rd axles

113 000

103 000

72 000

High severity – 4th axles

46 000

53 000

64 000

SBR/BR
Reference compound

80/20 NR/BR
High stearic semi-EV
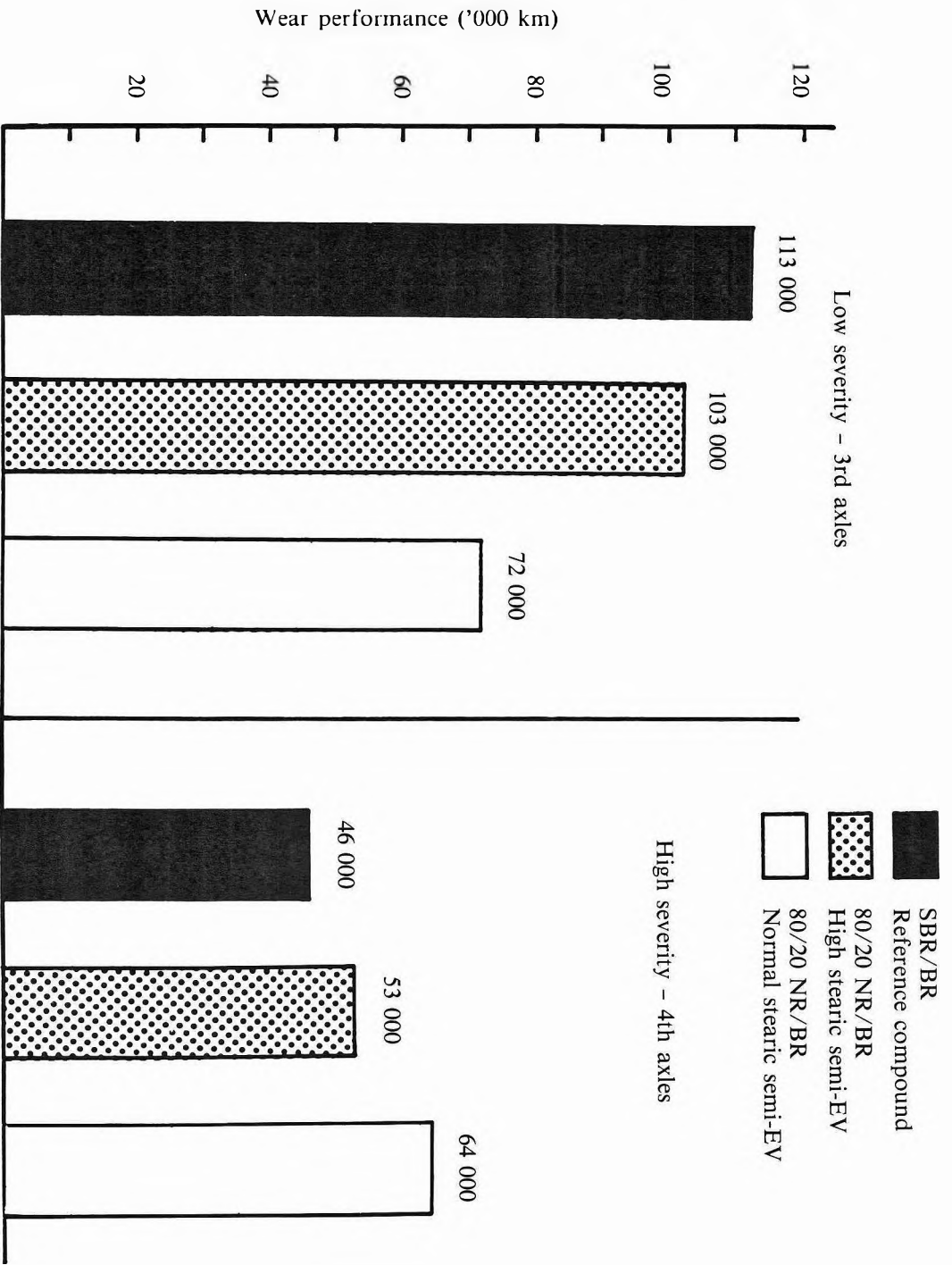
80/20 NR/BR
Normal stearic semi-EV

Figure 4. Wear performance of heavy-duty truck tyre retreads (first service trial).

to enhance abrasion. This is the subject of the second series of trials, but before that, it is interesting to note the wear *rate* of the compounds in the first series.

Obviously, wear performance was closely monitored during all stages of the trials, and *Figure 5* shows the wear rates of the three compounds under the low and high severity conditions. Under the low severity conditions, it is clear that the 80/20 NR/BR compound with the normal stearic acid semi-EV exhibits an increase in wear rate as mileage progresses. This indicates that thermal-oxidative degradation is the predominant factor in the abrasion mechanism here, especially since the thermally resistant high stearic acid formulation gives a stable wear rate. While this feature confirms the belief that the reversion characteristics of NR adversely affect the long-term tread life of NR-rich compounds, there has been no evidence that reversion is detrimental to abrasion resistance at the start of tyre life, which was another concept associated with NR in truck tyre retreads. Under high severity conditions, the superior reversion resistance of the high stearic acid semi-EV compound is seen to be of no advantage, the normal stearic acid formulation providing a 20% better wear rate. This observation supports previous work by Veith[4] that, under high wear rate conditions, a tensile/tear mechanism is the dominant factor in tread abrasion, and that crosslink structure is less important than in the case of low wear rate conditions.

As well as tread wear tests, the tyres from these three compounds were also examined on a rolling wheel test rig for heat generation and rolling resistance properties. The laboratory observation that the high stearic acid semi-EV 80/20 NR/BR compound exhibited lower heat build-up in the Goodrich Flexometer test was confirmed in the actual running temperature of the tyre treads. As seen in *Figure 6,* the improved heat generation characteristics of the high stearic acid compound become more pronounced at higher speeds. At 30 km per hour the high stearic acid NR/BR compound runs 8°C cooler than its normal stearic acid counterpart and 12°C cooler than the synthetic tread. This differential is increased to 21°C and 23°C respectively at 100 km per hour. This lower running temperature of the high stearic acid NR/BR compound may also be partly responsible for its improved tread wear performance for tyres under the low severity condition, where the thermal degradation appears to control the abrasion mechanism. Power consumption readings taken during these heat generation measurements were used to determine rolling resistance. While the normal stearic acid 80/20 NR/BR compound was observed to have only a small advantage in rolling resistance over the synthetic tread, the high stearic NR/BR formulation gave a 5% improvement in rolling resistance at 60-100 km per hour, which would lead to significant fuel savings over the total life-time of the retreaded tyre.

Second Service Trials

As mentioned above, the reversion resistant 80/20 NR/BR compound evaluated in the first series of service trials gave remarkably good wear performance compared to the synthetic reference compound, considering the latter contained 45 parts of BR. The obvious next development was to examine the effect of increasing the BR content of the NR-rich formulation, which is known to improve wear performance but at the same time reduce wet traction. A laboratory study was made of the properties of NR/BR vulcanisates containing from 20 parts to 50 parts BR. These suggested that the optimum BR content of the blend to provide the best compromise of wear and wet grip was 35 parts, and this blend was examined with the normal 55 parts of N339 black and also higher black/oil levels to similarly optimise on these two critical properties. The result was the two compounds shown in *Table 4* alongside the 80/20 NR/BR high stearic acid control from the original evaluation. These 65/35 NR/BR blends, with normal black (55 parts) and high black/oil (62/12) were vulcanised with the same high stearic acid semi-EV system, and possessed more than adequate reversion resistance requiring in excess of 2 h to exhibit 5% reversion. The DIN abrasion index suggested that both should out-perform the previous high
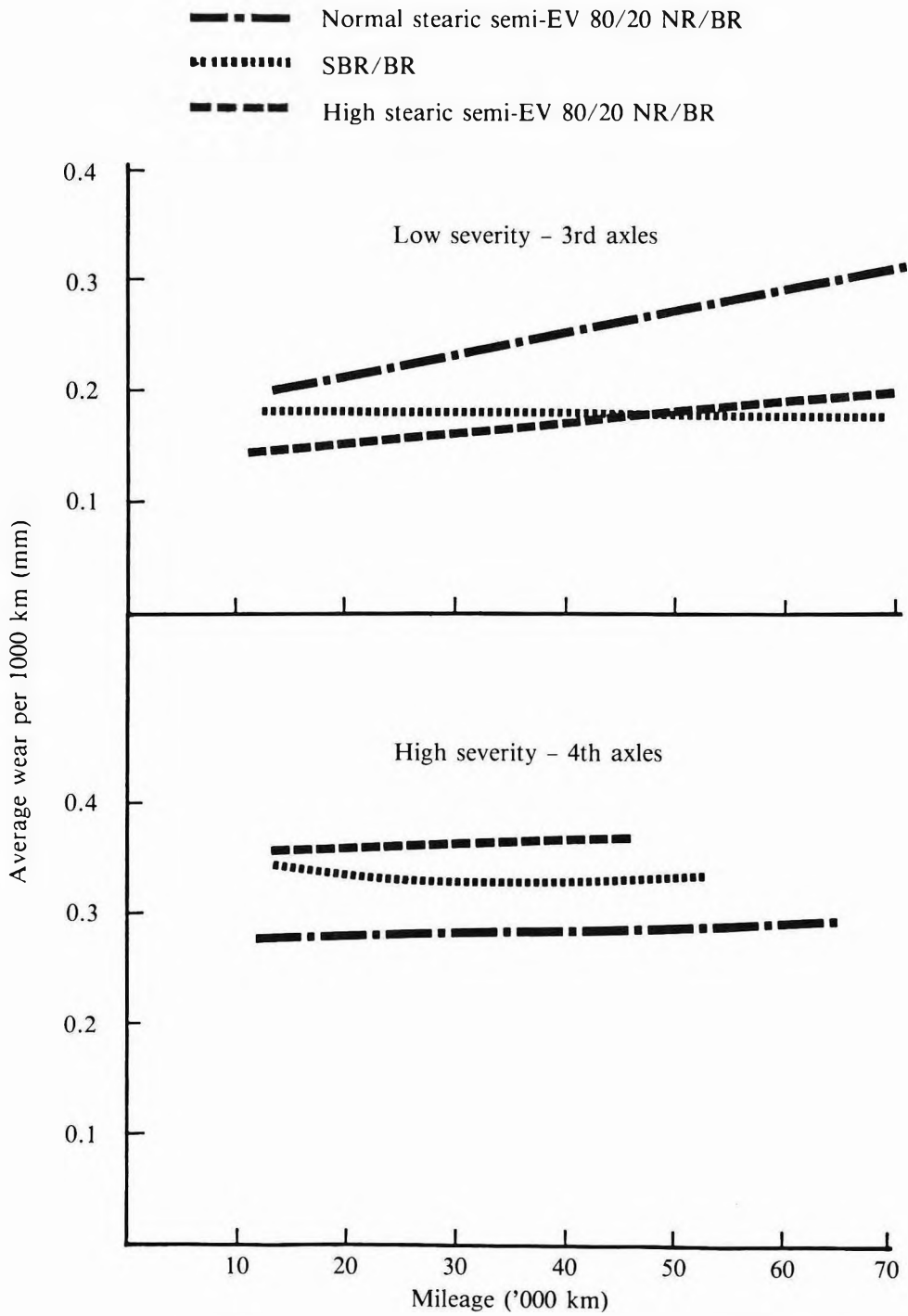
Figure 5. Wear rate of heavy duty truck tyre retreads (first service trials).
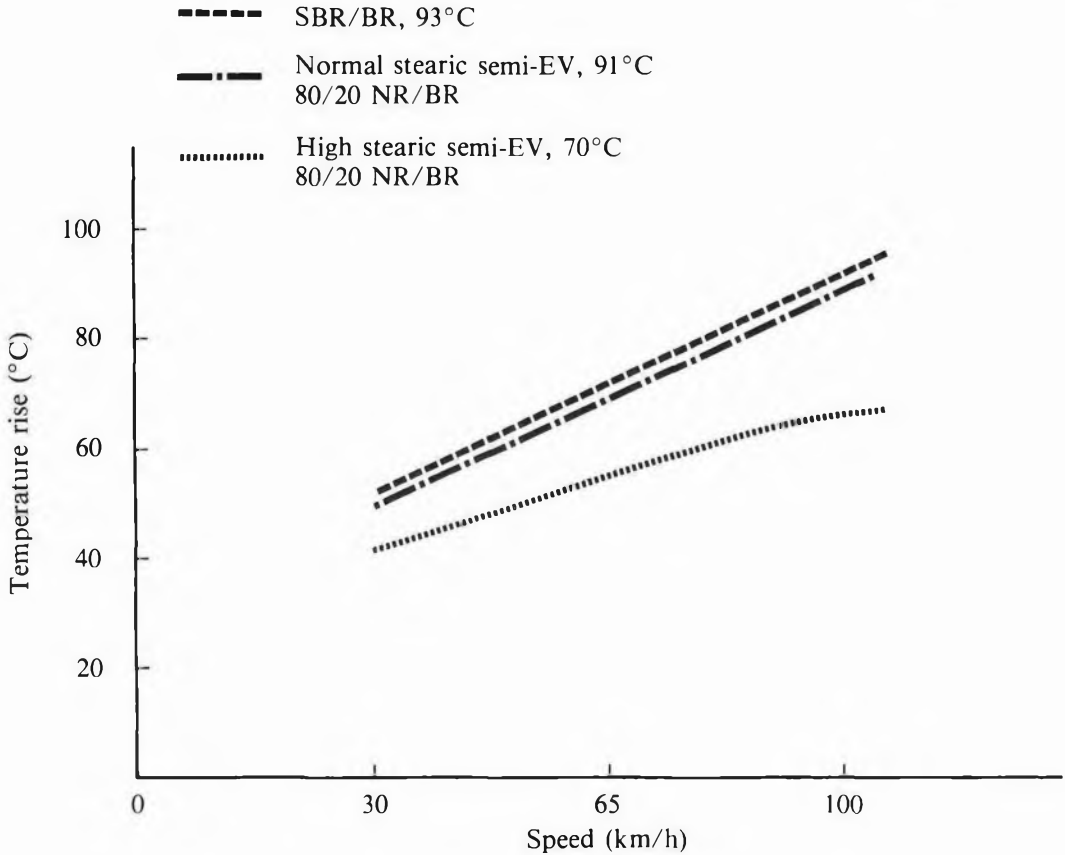
Figure 6. Heat generation of truck tyre retread compounds.

stearic acid 80/20 blend, and hence a second series of service trials was commenced in mid-1985 to evaluate their actual wear performance in truck retreads.

This second service trial was kept as close as possible to the first, using the same haulier, same vehicle type and same retreader. Again forty-eight 1100 × 22.5 heavy-duty radial truck tyres were retreaded by Vacu-Lug using the three compounds shown in *Table 4*. This gave an 80/20 NR/BR high stearic acid semi-EV formulation which was common to both series of trials, and hence could be used to interrelate the two. The distribution of these tyres between the six vehicles used for the trial was also similar to before *(Figure 7)* to enable eight tyres per compound to be fitted to both the third and fourth drive axles.

The trials, which were commenced in June 1985 and completed in September 1986, indicate as shown in *Figure 8* that the high black and oil 65/35 NR/BR formulation out-performs the SBR/BR reference compound (whose value here has been calculated *via* the common 80/20 NR/BR compound) under low severity conditions. The interesting observation is that the 65/35 NR/BR formulation with the normal black loading, which according to laboratory DIN abrasion should have out-performed the earlier 80/20 blend by 15%, in fact on the road only showed a 6.5% improvement. In contrast, the high black and oil 65/35 compound, which should have been inferior to the normal black compound according to the laboratory data, in fact showed a 23% improvement over the 80/20 blend on the road. This indicates the utmost importance of real service trials.

TABLE 4. TREAD COMPOUNDS FOR HEAVY DUTY TRUCK TYRES (SECOND STUDY)

Item	80/20 NR/BR 1984 control	65/35 NR/BR Normal black	65/35 NR/BR High black/oil
Tread compounds			
SMR 20	80	65	65
Med cis 1,4 BR	20	35	35
Struktol 40MS	4	4	4
N 339 black	55	55	62
High aromatic oil	8	8	12
Zinc oxide	4	4	6
Stearic acid	6	6	6
Antidegradant	2	2	2
Sulphur	1.2	1.2	1.2
MBS	1.2	1.2	1.2
Monsanto rheometer (150°C, 1° arc, 50 range)			
t_{max} (min)	40	45	38
$t_{5\%R}$ (min)	120 +	120 +	120 +
Vulcanisate properties (22 min/150°C)			
DIN abrasion index	109	125	118
Modulus at 300% (MPa)	9.7	9.4	9.9
Tensile strength (MPa)	23.6	23.3	21.5
Elongation at break (%)	557	588	533
Hardness (IRHD)	62	67	68
Tear, trouser (kN/m)	13.4	24.3	14.8
Resilience, Dunlop (%)	58	57	53
HBU, Goodrich (T°C)	63	69	80

The substantial difference between the severity of the two drive axles in these vehicles is also of great concern, since in the fourth axle high severity position, the high black/oil 65/35 NR/BR compound gave inferior mileage compared to both the normal black/oil and the 80/20 compounds. In order to study this wear-severity aspect further, retreads from the same three compounds were also examined on the second steer axles which would be expected to be another position of low severity. Here the high stearic normal black 65/35 NR/BR compound gave an average tread life of 140 000 km compared to that of the 80/20 compound which lasted 106 000 km. However, the high black/oil 65/35 NR/BR compound only gave an average life of 80 500 km, well below that of the other NR-rich compounds. Thus, in this position, the normal black/oil 65/35 blend confirms the laboratory DIN abrasion results of improved wear over the 80/20 NR/BR blend, while the high black and oil compound does not. The importance of severity cannot be overlooked and it does not appear from these results that laboratory DIN abrasion can be easily correlated to either high or low severity conditions on the road. The additional testing on second steer axles confirms that improved mileage can be obtained by the use of a 65/35 NR/BR blend rather than an 80/20, but it is not consistent with the drive axle results, which in the low severity position suggest that the high black and oil compound provides significantly higher mileage.
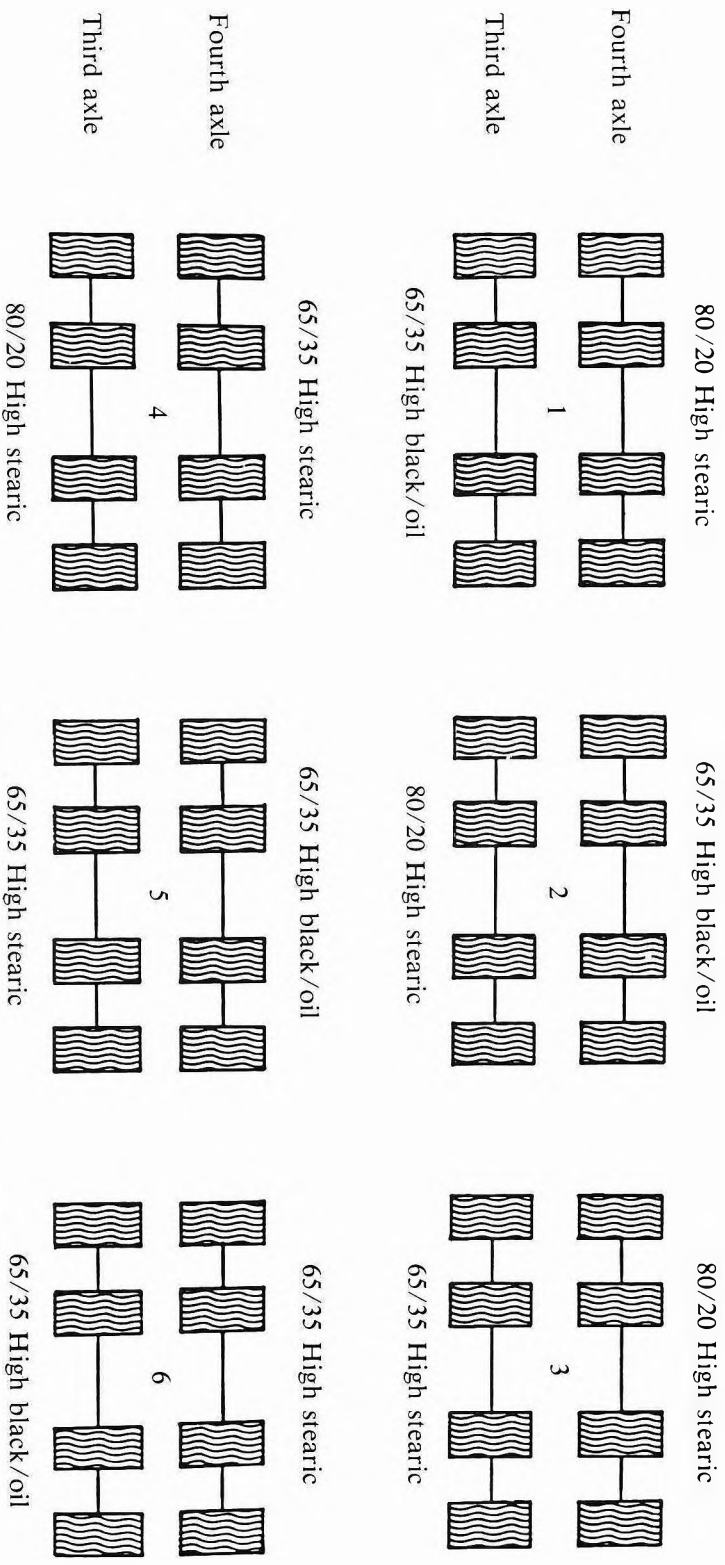
Figure 7. Heavy-duty truck retread fitting arrangement (second service trial).
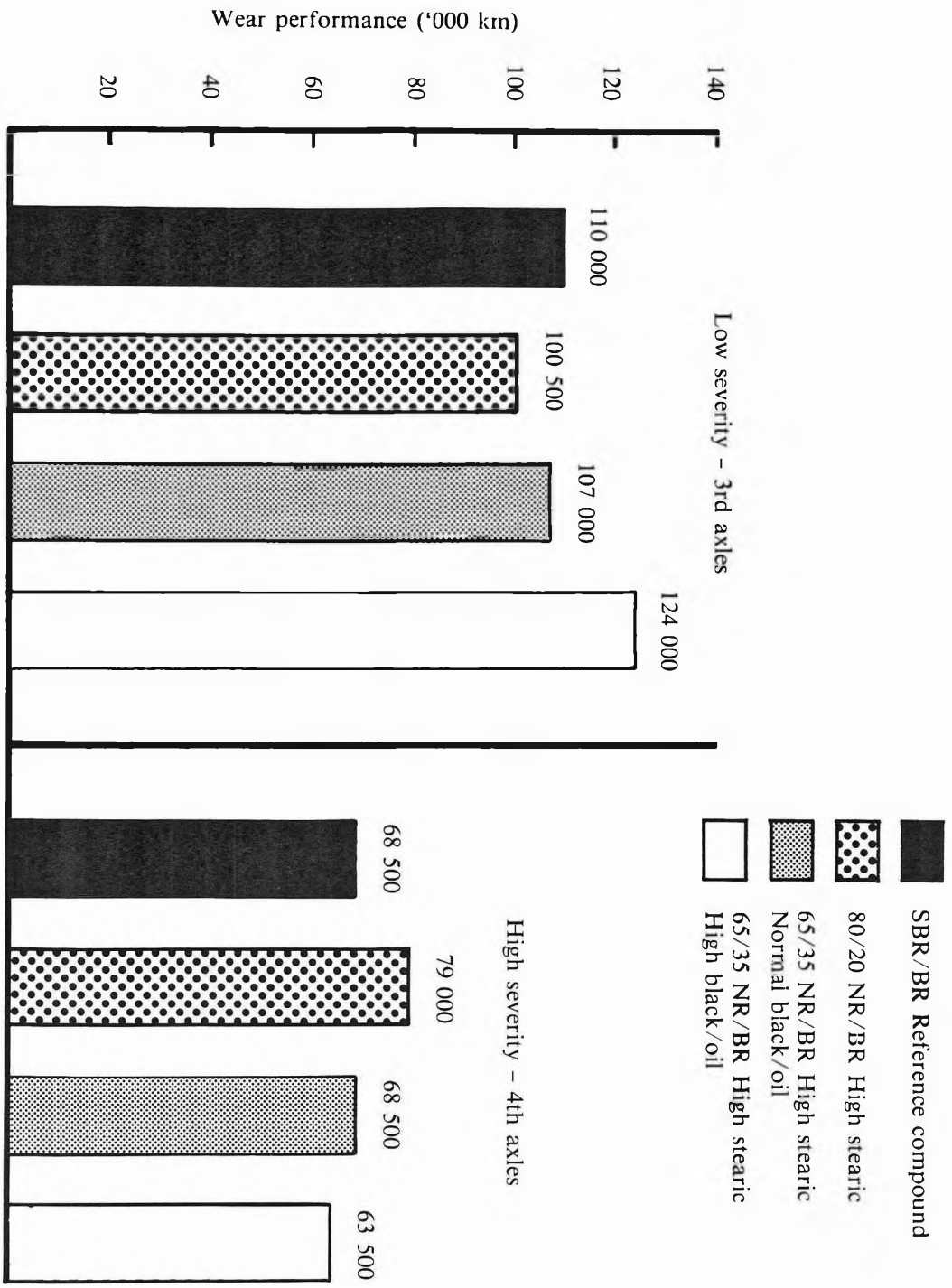
Figure 8. Wear performance of heavy-duty truck tyre retreads (second service trial).

Wear performance ('000 km)

Low severity – 3rd axles

110 000
100 500
107 000
124 000

High severity – 4th axles

68 500
79 000
68 500
63 500

SBR/BR Reference compound

80/20 NR/BR High stearic
Normal black/oil

65/35 NR/BR High stearic
High black/oil

65/35 NR/BR High stearic
High black/oil

Considerably more extensive testing will therefore be required to establish the best overall NR-rich truck retread compound for all wear conditions.

CONCLUSION

The discovery of a reversion resistant high stearic acid semi-EV system for NR-rich truck retread compounds has been shown by service trials to give much improved wear performance compared to a normal stearic acid formulation. In the first series of trials, an 80/20 NR/BR compound with this cure system came to within 10% of a standard high mileage synthetic compound containing 45 parts BR under low severity wear conditions, and outlasted it under high severity wear conditions. In a second trial, a 65/35 NR/BR compound with the same cure system, and higher black and oil, would appear to have potential to out-perform the synthetic compound under low severity conditions. The 80/20 NR/BR compound also exhibited low heat generation characteristics in the tread, and showed 5% better rolling resistance than the synthetic tread which would result in long-term fuel saving.

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