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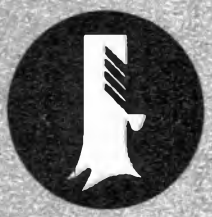

JOURNAL OF NATURAL RUBBER RESEARCH

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Surface Treatment of Rubber to Reduce Friction

A.D. ROBERTS* AND C.A. BRACKLEY*

Traditional methods for reducing the surface friction of rubber articles are reviewed and explored experimentally. Results of simple friction tests are given for various treatments. These include halogenation, oxidation and acid attack. The general conclusion is that the treatments cause surface roughening which will contribute to reduced friction.

The aim of many surface treatments of rubber, traditionally performed by wet chemical attack, is to reduce the surface tack and sliding friction of rubber articles, such as sheeting, liners and wipers. The problem in industry is to perform this simply and safely.

This study presents the results of simple friction tests for various surface treatments. The treated rubber samples have all been compared in an identical way by rubbing against a glass plate possessing small undulations in its surface ('wavy' glass). Not only are initial friction coefficients compared, but also any change in value with continual rubbing (durability test). The results show that a range of friction levels can be obtained according to the treatment employed, and that different treatments have different durabilities.

REVIEW OF TREATMENTS

Natural rubber (NR) is very reactive towards the halogen elements, acids and some organic halogen-containing compounds. Reactions with these are generally complex, involving both addition and substitution. Cyclisation of the rubber molecule may ensue, but the detailed chemistry of many of the reactions is not known even though halogen reagents were among the first with which NR was treated many years ago[1,2]. In the case of chlorine, if its content after reaction is less than 40%, the product is still soft and flexible, but when 65% is reached rubberiness is lost. The fully chlorinated material is hard and probably has a cyclic structure[3]. Some details about the reaction chemistry are available[4,5,6]. Chlorinated rubber can be obtained by directly treating sheets of rubber, rubber in solution or latex with chlorine gas. Hydrogen chloride gas adds readily to NR. The product remains flexible if the chlorine content is less than 30%; but above this figure, it is hard and brittle.

Hypochlorous acid reacts with NR in solution but the chlorine content of the products is higher than expected from simple addition, suggesting substitutive chlorination of the rubber by free chlorine present in the reagent. The use of bleaching powder to reduce the surface tack of rubber was described long ago[7] and was once more widely used than nowadays. When chlorine water or bleaching powder is used, the strength of the reagent and time of exposure require careful control to avoid excessive hardening of the rubber surface. Typically, the reagent solution should contain about 0.3% free chlorine and exposure is about 2 min. It is reported[8] that further treatment of the hypochlorinated rubber surface with oxalic acid solution can decrease the friction coefficient and prevent corrosion of contiguous metal parts.

More complex ways have been reported for introducing chlorine into a rubber surface. A chemically resistant, less frictional surface is claimed[9] by treatment with a chlorine gas-sulphur dioxide mixture in the presence of

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ionising radiation. Alternatively, changes occurring to NR by the action of chlorosulphonyl isocyanate have been described[10]. The use of concentrated hypochlorous acid containing an oxidising agent has been patented[11] to make rubber surfaces resistant to abrasion. On a wider point, quite how these and other chlorinated rubber surfaces age is something yet to be fully explained.

Fluorine gas reacts violently with NR, but products containing up to 30% fluorine have been obtained which are rubber-like. For example, articles such as surgeons' gloves can be treated[12] by extending their surface by 10% by inflating with a fluorine/nitrogen gas mixture. Alternatively, a rubber mix may be treated with a fluoro-organic compound and after vulcanisation the article placed under reduced pressure to subject it to glow discharge[13]. Its surface will then have a low friction coefficient and enhanced wear resistance. Another way would be to treat a rubber surface with gaseous antimony pentafluoride in nitrogen gas as carrier[14]; thus treated friction coefficients are claimed to decrease by a factor of six times. Other ways are by fluoroplastic-containing lacquers applied to a rubber surface[15] or by surface grafts[16].

Anhydrous hydrogen fluoride has a powerful cyclising action on rubber. At low temperatures ($-150°C$) cyclisation can be suppressed and addition of HF to the double bond is obtained, the product containing 16% fluorine. It is rubber-like although weak, but ages well.

When NR is treated in solution at low temperature with bromine, the element adds to the double bond with very little substitution. Surface treatment with bromine water has been used to impart surface hardness to certain rubber articles such as windscreen wiper blades. The effect of bromination on the surface properties of rubber has been reported[17,18]. The addition of hydrogen bromide to the rubber molecule proceeds similarly to that of hydrogen chloride.

No well defined iodinated derivatives of rubber have been reported. The addition of hydrogen iodide has been but little studied. Interestingly to note, in 1961 the use of peracetic acid to remove surface tack on rubber was recommended by a food company[19] as a substitute for halogenation because it was claimed to be as good, but safer. There have been many attempts to substitute halogenation for something else. For example, the following may be cited: grit blasting[20], Teflon coating[21], molybdenum disulphide[22], graphite powder or paint[23], ultraviolet light to produce surface hardening[24] or polymer grafts[16,25,26], metal plating[27,28], surfactant treatment[29], glow discharge/plasmas in vacuum[30,31].

The main object of surface chlorination of rubber articles is to reduce their dry friction, often against glass. A bonus is that it can also slow down surface ageing. Frequently, a surface treatment is simply described in terms of a reduction in friction and little said about the physico-chemical nature of the modified surface. Studies by scanning electron microscopy (SEM) made sometime ago[32] showed that chlorination increases the fine scale roughness of a rubber surface, with a corresponding decrease in dry friction. More recently, the chemistry of chlorine addition has been examined by XPS and the physical effects of chlorination on surface morphology noted[33].

Two other classes of chemical treatment of rubber surfaces must be mentioned. Sulphuric acid has been used to reduce the tack of raw rubber. It renders the surface hard and micro-rough[34]. Vulcanised rubber sheets have been treated with dilute sulphuric acid to improve their anti-blocking properties[35]. An extension of this comprises treating with an aqueous solution containing an aromatic sulphonic acid[36]. The other treatment is based on permanganate. Some time ago, a study was made of the products of surface reaction of aqueous acidified potassium permanganate with NR[37].

EXPERIMENTAL

The frictional force between a rubber sample (treated or not) and 'wavy' glass was measured using simple apparatus. This consisted of a rubber hemisphere fastened to the traverse stage of a microscope, the traverse being driven by

an electric motor. To the top of the rubber hemisphere was fixed the rubber sheet sample under test. It was laid over the hemisphere and held in place at its edges with sticky tape. The 'wavy' glass plate was part of a lever arm and rested under an applied load on the rubber test sample *(Figure 1)*. The applied load was 4 N, which gave a contact circle of diameter 10 mm with untreated rubber. When treated rubber was used there was no well defined contact periphery. The sliding distance was 27 mm and this was traversed at a fixed nominal speed of 1 mm per second, the motion being to and fro, with the aid of a reversing switch. In this way, durability of the surface treatment could be assessed.

The friction force between rubber and glass in the horizontal plane was detected by strain gauged leaf springs on the lever arm. Strains were measured on a suitable electric bridge, the output amplified and displayed on a chart recorder. The leaf springs were calibrated by applied forces in the horizontal plane, so that displacements on the chart recorder were known in terms of force. Friction coefficients were then taken as that force divided by the applied normal load.

The NR sample vulcanisates used were formulated as indicated *(Table 1)* and moulded as 1 mm thick sheet. Rubber hardness was measured on a suitable meter. From the IRHD value, Young's modulus, E, was directly found from an established curve of the variation of E with IRHD. Glass transition temperatures were measured by differential scanning calorimetry. The moulded rubber samples were cut to size (about 400 mm^2) for friction tests. Cut samples were cleaned with pure acetone. This consisted of wiping a surface with cotton wool soaked in acetone followed by brushing to remove residual matter, the brush having been dipped in acetone. Thus cleaned, samples were either directly friction tested or surface treated. When treated, any residues were rinsed away with de-ionised water and the surface dried in a stream of cool air. Thereafter, the surface was friction tested at room temperature.

To treat the surface of rubber samples chemically involved their immersion in appropriate aqueous solutions. The solutions were stirred during treatment. The compositions of solutions used are given for reference *(Table 2)*, though minor variants are likely to produce similar results.

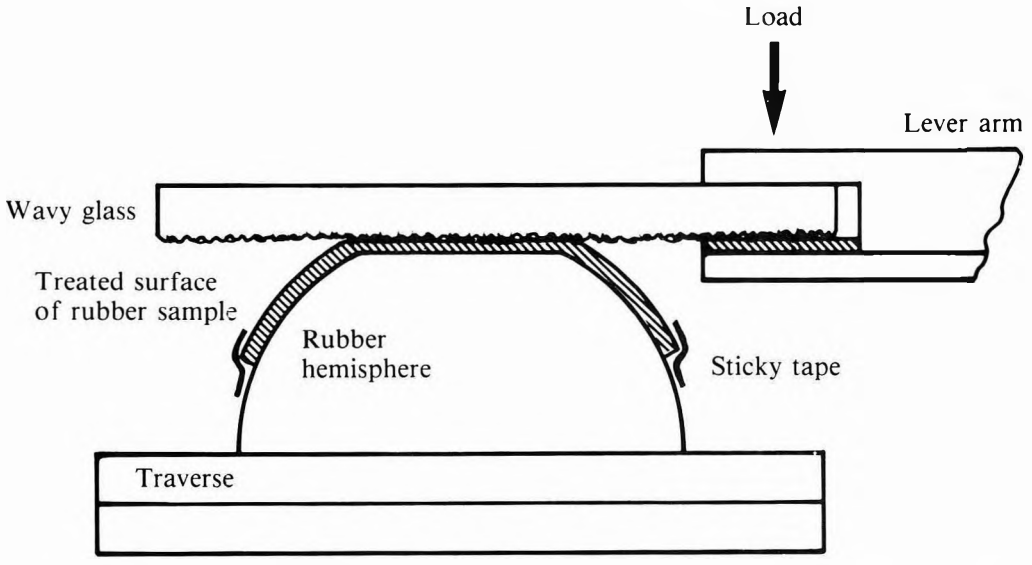


Figure 1. Sliding contact arrangement for assessing various surface treatments of sheet rubber samples. Sheet thickness ca. *1 mm, rubber hemisphere diameter 37 mm.*

TABLE 1. RUBBER SAMPLE FORMULATIONS

Compound	Formulation (parts by weight)		
	A	B	C
NR (SMR L)	100	100	100
Zinc oxide	5		5
Stearic acid	2		2
Flectol H	1		
Santoflex 13	2		
Dicumyl peroxide		1	
Sulphur	0.5		2.5
Sulphasan R	2		
MOR	1		
Robac P2	0.2		
N672 SRF black	60		
Nonox ZA			1
Santocure NS			0.5
Cure time (min)/temp (°C)	24/150	60/150	40/140
Hardness (IRHD)	66	29	44

TABLE 2. COMPOSITION OF TREATMENT SOLUTIONS

Reagent	Solution								
	1	2	3	4	5	6	7	8	9
Sodium hypochlorite aq. sol. (14% Cl) (ml)	5								
Concentrated hydrochloric acid (ml)	2								90
Water (ml)	200	100	100			50	80		
Bromine (ml)		5							
Potassium iodide (g)			10						
Iodine (g)			1						
Potassium permanganate (variable concentrations in water)				10^{-4}M to 10^{-1}M					
Sulphuric acid (ml)				10^{-2}M	10^{-2}M	50			
Potassium dichromate (aq. sol.)					10^{-2}M				
Concentrated nitric acid (ml)								30	
40% Peracetic acid (ml)							20		
Hydrogen peroxide (ml)									25
90% Formic acid (ml)									5

RESULTS

Surface Chlorination

The traditionally preferred method for reducing tack and friction may be regarded as chlorination, usually by hypochlorite solution or chlorine water (gas bubbling). We have friction tested after using the hypochlorite method *(Solution 1, Table 2)*. Rubber samples were suspended in the treatment solution for 3 min neutralised with 2% ammonia, rinsed in distilled water and dried with cool air. Results for a gum and a carbon-filled NR vulcanisate *(Figure 2)* show that chlorination produces about a three- to four-fold decrease in initial sliding friction. Friction levels for the two samples of carbon-filled vulcanisate are different because in one case the surface was very slightly talced beforehand. Traces of talc were present before chlorination, and on the untreated sample. Surprisingly, at long rubbing times, the differences between treated and un-

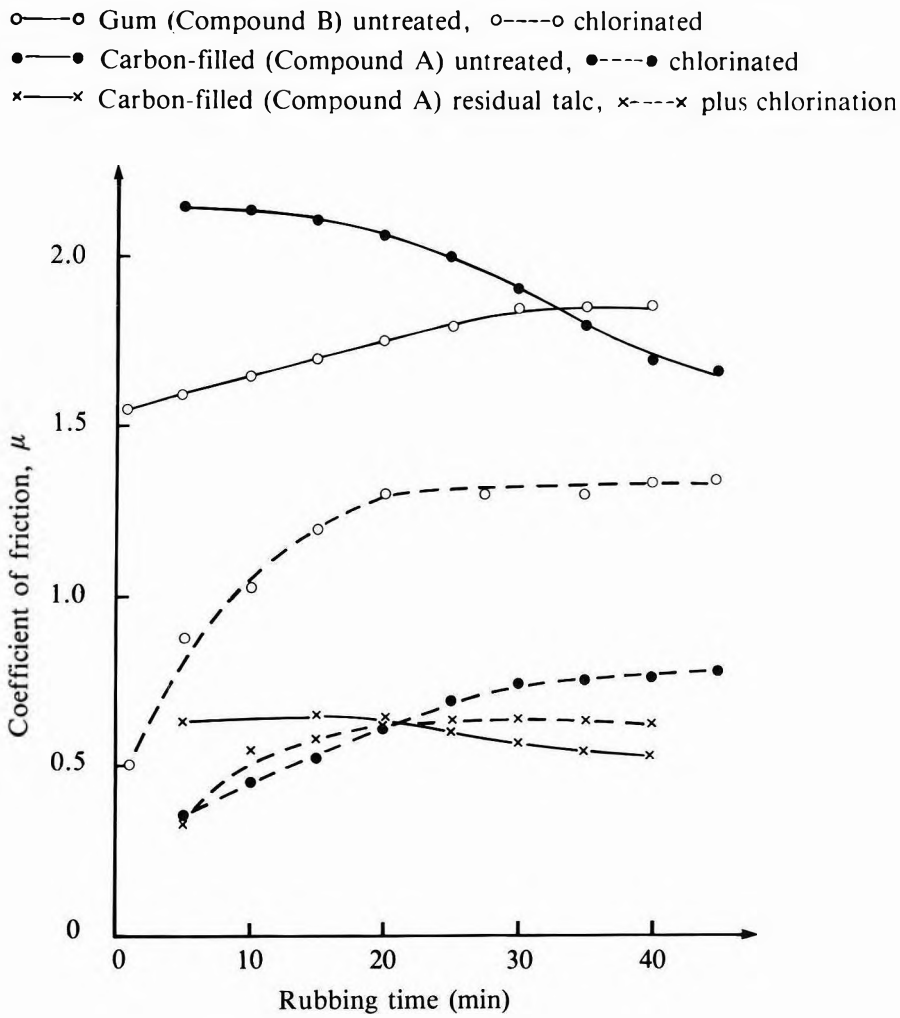


Figure 2. Effect of surface chlorination on the dry sliding friction of gum and carbon-filled NR vulcanisates in reciprocal movement against 'wavy' glass.

treated rubber surfaces diminish. Untreated gum rubber friction increases with rubbing time probably due to the enlarged contact area, whereas untreated carbon-filled rubber decreases due to surface roughening caused by abrasion. Talc alone has a marked effect in reducing the friction of untreated rubber.

Other Halogens

A saturated solution of bromine *(Solution 2, Table 2),* was used to treat rubber samples for 3 min. Thereafter, the sample surfaces were neutralised with 5% ammonia, rinsed with distilled water and blow dried with cool air. The brominated samples were then friction tested.

To iodinate sample surfaces, the same method as above was employed with treatment *Solution 3 (Table 2).* Fluorination was carried out by Bettix Ltd (UK) using their patent process.

A comparison of all the halogens for gum and carbon-filled rubber is shown in *Figures 3* and *4.* Fluorination of gum rubber resulted in very low friction and good wear resistance; but for carbon-filled rubber, bromination gave the lowest friction.

Oxidation

Previous work[37] has shown that a polyglycol film is formed on the surface of NR when

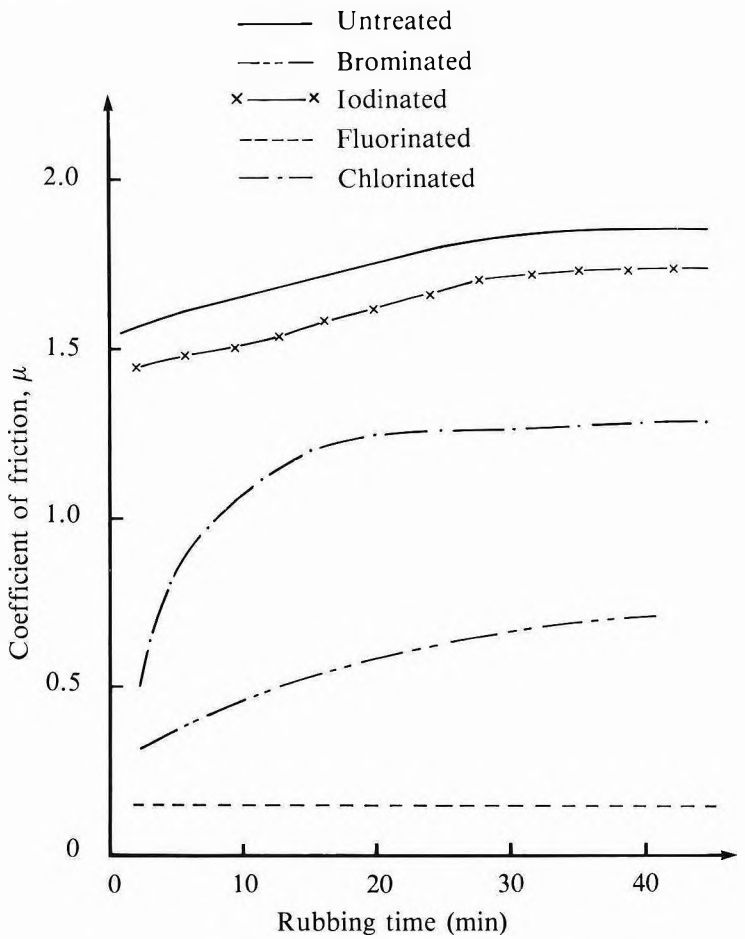


Figure 3. Comparison of halogen treatments for gum NR vulcanisate (Compound B).

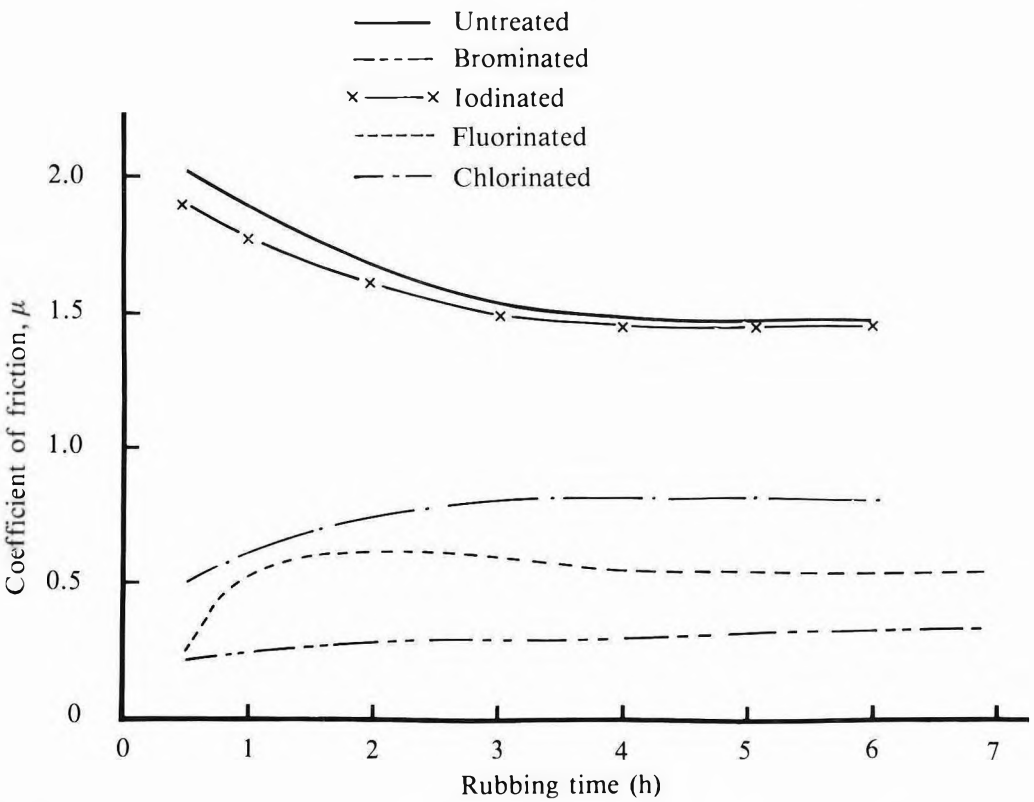


Figure 4. Comparison of halogen treatments for carbon-filled NR vulcanisate (Compound A).

treated with dilute acidic potassium permanganate. Unless the permanganate concentration is very low, other oxidative scission reactions occur at the same time. Tests were undertaken to determine the treatment effect of various permanganate concentrations in 0.01*M* sulphuric acid.

A slightly modified experimental arrangement was employed to that shown in *Figure 1*. A sulphur-cured rubber *(Compound C, Table 1)* moulded as a 25 × 25 mm square flat 10 mm thick was first abraded with silicone carbide paper (Tri-M-ite 180E) in a 'standard' manner. After acetone cleaning and surface roughness measurements (Talysurf 10) had been taken, the flat was fixed to the friction lever arm and slid under a load of 10 N against 'wavy' glass. Thereafter the flat was removed and placed in permanganate treatment solution *(Solution 4, Table 2)* for a given time, then rinsed, dried and the friction and surface roughness re-measured. The test was repeated for different treatment times and permanganate concentrations by re-abrading the rubber to expose fresh surface. Results showed that permanganate treatment increased the surface roughness *(Table 3)* according to solution concentration, and the friction measurements showed a corresponding fall in level *(Figure 5)*. This may be interpreted as a fall in friction with increasing surface roughness.

Rubber samples soaked in permanganate solutions acquired a patchy purple coating and a black residue could be rubbed off. In view of this, durability tests were carried out. The rise in friction with just a few to and fro traversals against wavy glass was noticeable (*Figures 6* and *7*). Even so, in the longer term, the rate of rise in friction diminished and the level remained below that of an untreated surface.

TABLE 3. EFFECT OF PERMANGANATE TREATMENT ON SURFACE ROUGHNESS

Permanganate concentration (M)	Immersion time (min)	Talysurf (μm CLA)	Roughness (% increase)
None		3.58	
10^{-4}	30	3.70	3.3
10^{-3}	9	3.80	5.3
10^{-2}	2	3.95	8.8
10^{-1}	0.5	4.05	13.1

Treatment solutions were various molar strengths of $KMnO_4$ in 10^{-2}M H_2SO_4.

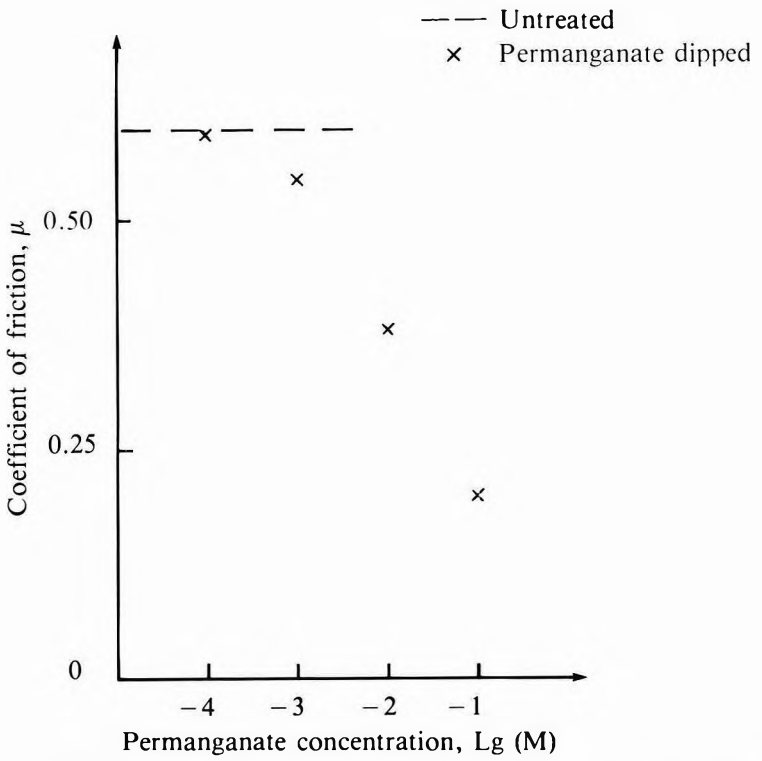


Figure 5. Surface treatment of gum NR vulcanisate (Compound C) *with acidified solutions of potassium permanganate.*

For comparison, the effect of potassium dichromate as oxidant was tried *(Solution 5)*. The rubber sample was treated in the same way as for permanganate solution. The friction results *(Figure 6)* suggest it is less effective than permanganate.

Acid Attack

The effectiveness of various concentrations of sulpuric acid was investigated. Results for 3 min immersion of 1% dicup NR samples in acid *(Figure 8)* show a considerable fall in

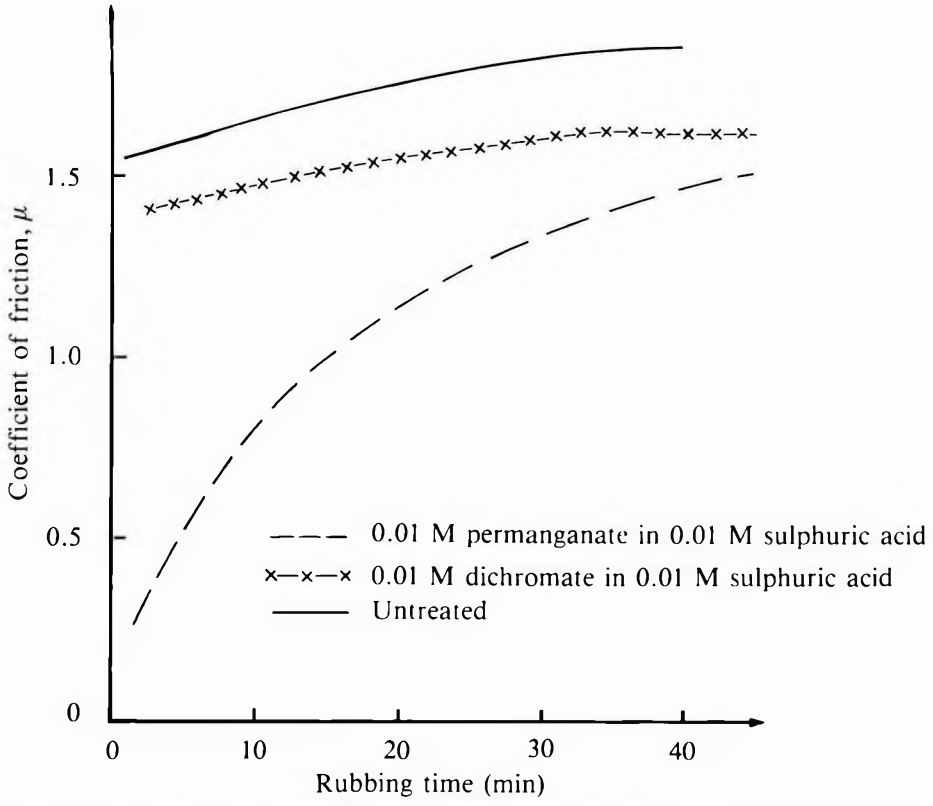


Figure 6. Comparison of oxidising agents for the surface treatment of gum NR vulcanisate.

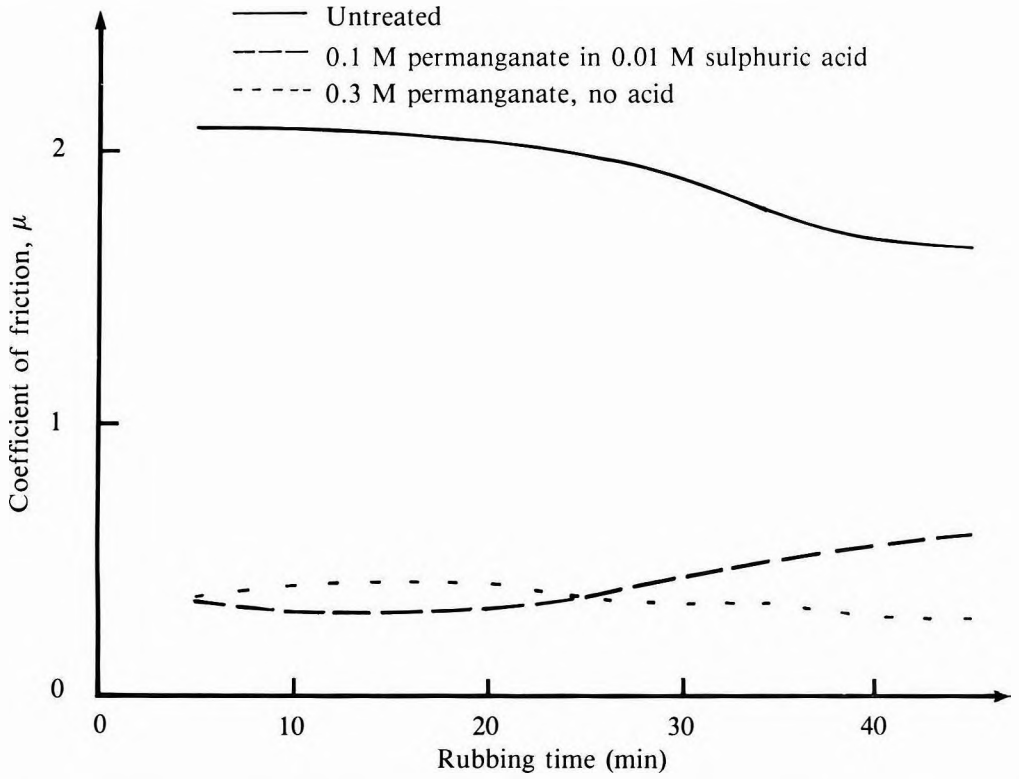


Figure 7. Surface treatment of carbon-filled NR vulcanisate (Compound A) *with potassium permanganate solutions.*

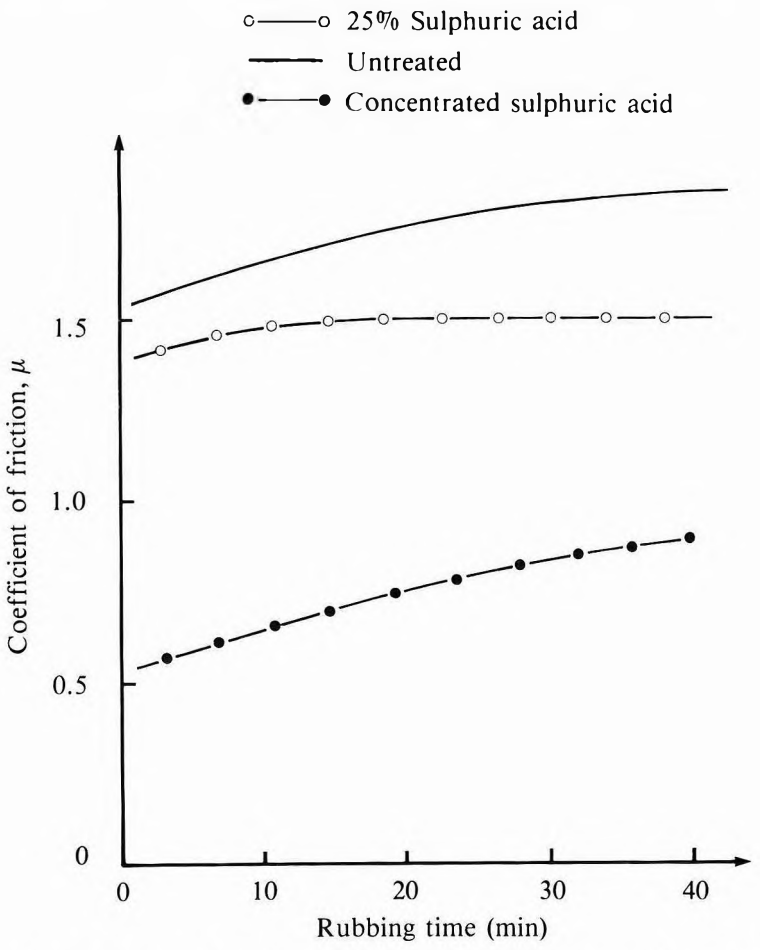


Figure 8. Sulphuric acid treatment of gum NR vulcanisate (Compound B).

friction for concentrated acid, but much less when the acid is dilute.

The effect of some acids on very slightly talced carbon-filled rubber was examined. Immersion times varied, as indicated *(Figure 9)*. All treated samples were rinsed with water, neutralised in ammonia, rinsed again with distilled water and dried at room temperature. The friction of the untreated rubber appears surprisingly low. This is probably due to residual talc particles. The high initial friction with nitric acid may be due to the dissolution of residual talc. Clean, untalced carbon-filled rubber showed higher levels of friction *(Figure 10)*.

Surface Coating

Some rubber samples were coated with 'Satreat' halogen primer[38] which was scrubbed onto surfaces with a stiff bristled brush. Any residue was removed with 25% ethanol. Samples so treated were smooth to touch, had a 'milky' appearance and gave low friction *(Figure 10)*. Whether it is physical roughening by brushing, or halogen attack, that reduces the friction, is not clear.

Samples were PTFE coated (Fothergill Engineered Surfaces Ltd) using an air cure resin based system. Coated surfaces were smooth to the touch, but the coating cracked when rubber

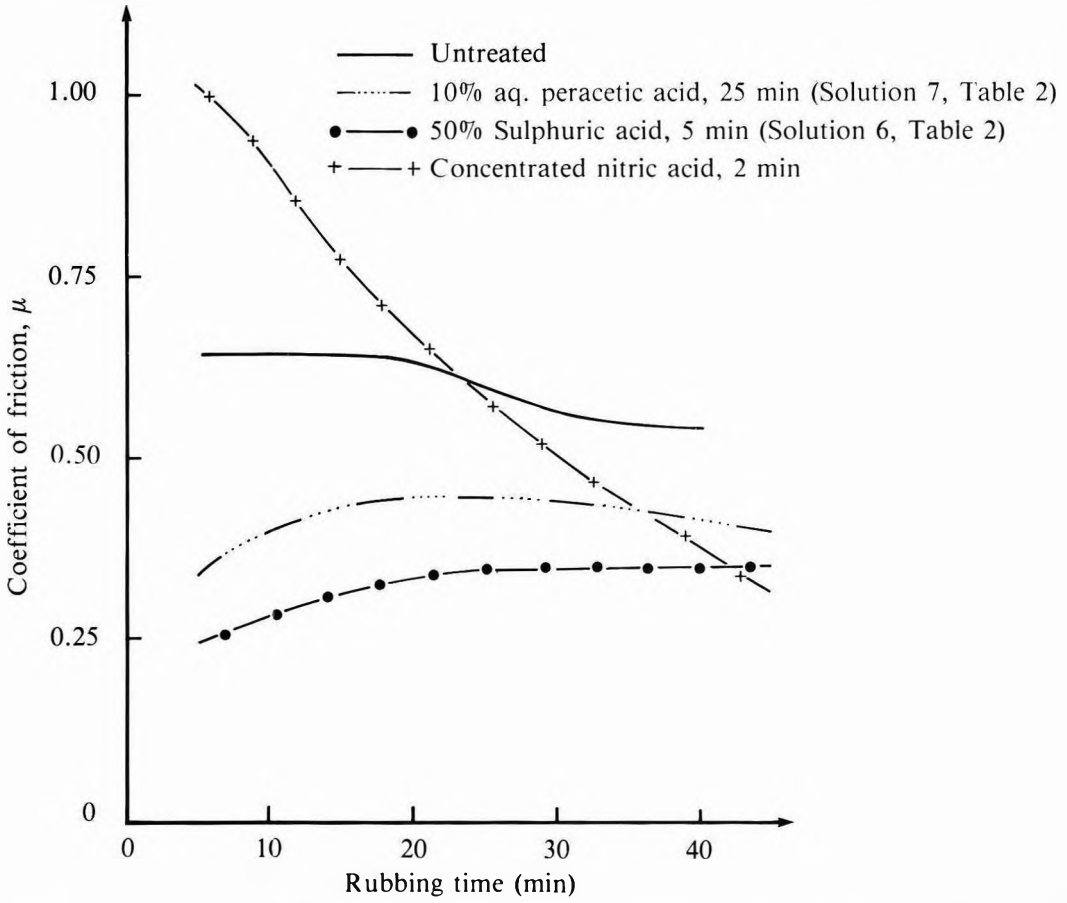


Figure 9. Attack by various acids on slightly talced carbon-filled NR vulcanisate (Compound A). *Immersion times in acids are as indicated.*

samples were flexed or stretched. Although the friction was low *(Figure 10)* and the wear resistance good, the coating could be all too easily stripped off with sticky tape.

Ageing

It is generally believed that for exposed rubber articles during their working life time chlorine in their surface skin eventually becomes replaced by oxygen without loss in low friction. Exactly what happens on ageing is not clear. Earlier work[39] has shown that photo-oxidised rubber (achieved by placing sample in direct sunlight) acquires a hardened skin and its friction coefficient can fall to the order of 0.2. In this study, we have attempted to examine the effects of ageing upon friction of chlorinated rubber surfaces by either heating them in an oven or exposing them to direct sunlight (in and outdoors).

Carbon-filled samples *(Compound A, Table 1),* some chlorinated several weeks before, were aged by heating at 120°C in an oven for 15 min. It is noted that the chlorinated samples had been stored in a polybag in the dark for several weeks and during this period displayed a low value of friction coefficient. After heat ageing all samples were immediately friction tested. The results indicate *(Figure 11)* reduced friction, even for chlorinated samples, though brominated surfaces showed no change after heating. The surface roughness of heat

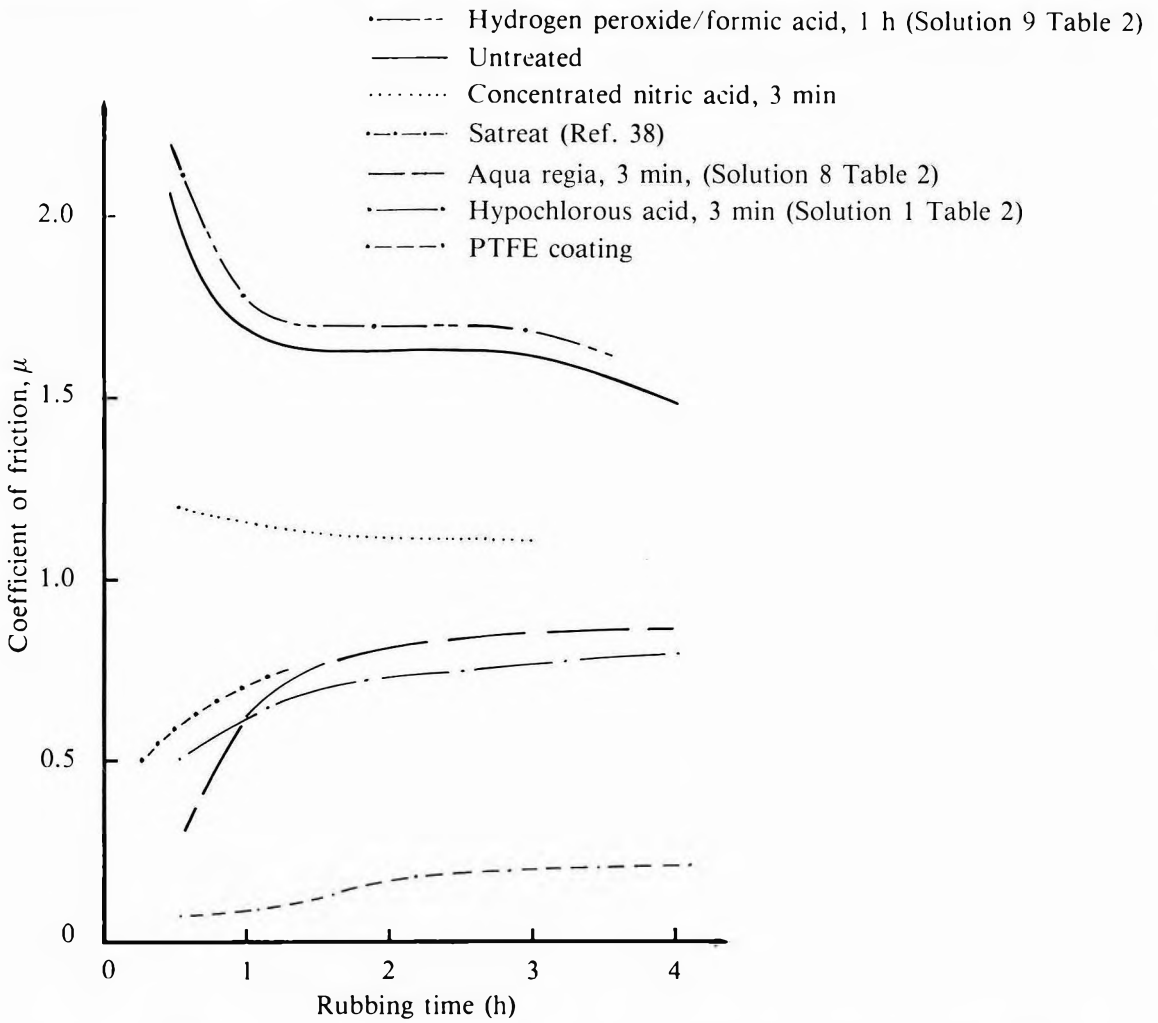


Figure 10. Various coatings and acid treatments of clean, freshly prepared, carbon-filled NR vulcanisate samples (Compound A). *Immersion times of samples in acids are indicated.*

aged samples was measured (Talysurf 10) and found to be greater than unaged samples *(Table 4)*. This may, in part, explain the fall in friction caused by heat ageing.

The effect of light exposure in air (photo-oxidation) was studied for carbon-filled samples *(Compound A, Table 1)* in two ways. The simplest involved measuring the friction of chlorinated and untreated rubber samples before and after placing them on an indoor window-sill in the sun. The change in friction was followed with the time of exposure. More complex was the setting-up of samples outdoors on an inclined (45°) board facing south and unprotected from wind and rain. In all cases, the friction fell with increasing exposure time *(Figure 12)*. Conversely, the surface roughness tended to increase with exposure time *(Figure 13)*. It was interesting to find that for outdoor exposure, chlorinated and untreated samples gave the same low level of friction after a couple of weeks.

When a plot is made of friction coefficient against surface roughness all the above results

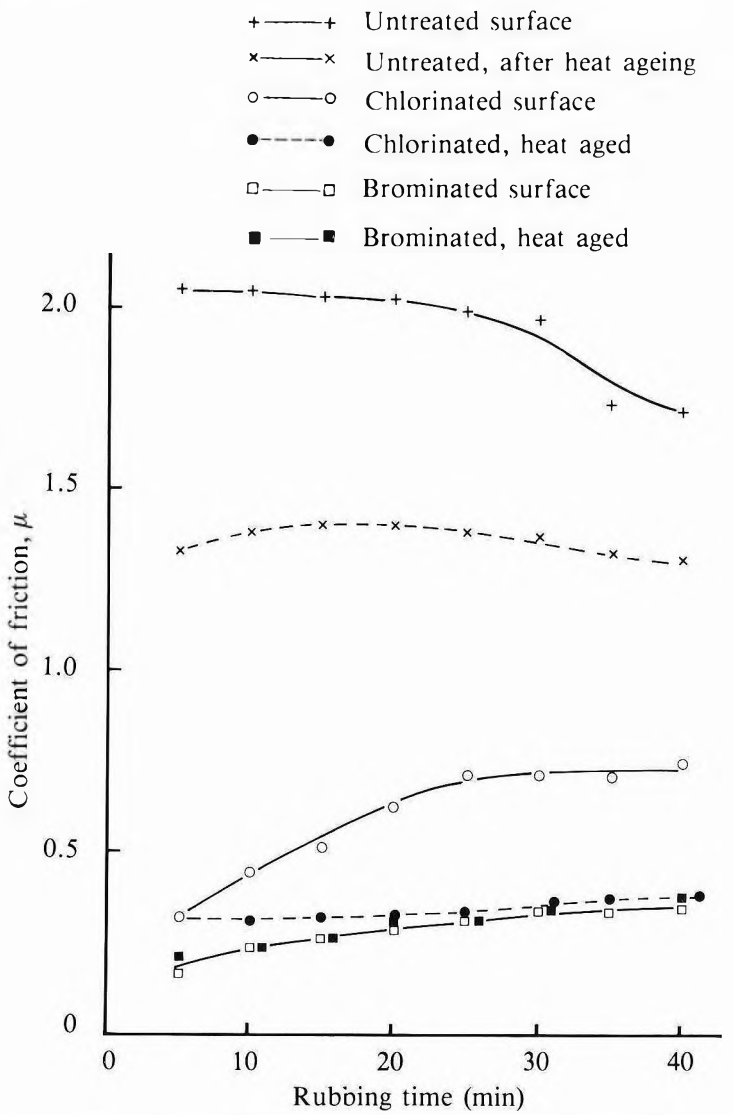


Figure 11. Heat ageing of surface treated and untreated carbon-filled NR vulcanisate (Compound A).

for heat ageing and sunlight exposure fall on the same curve *(Figure 14)*. This is strong evidence for the role played by surface roughness in reducing the level of sliding friction, whatever the way of ageing.

Additional outdoor sunlight exposure tests were carried out on unprotected rubber samples *(Compound B, Table 1)*. Not unexpectedly, these degraded quite quickly, but it was interesting to see that surface chlorination of such samples delayed degradation by a factor of four in time *(Table 5)*.

ANALYSIS

Surface analysis of chemically treated rubber samples was made by using a profile machine (Talysurf 10) and by examination with a scanning electron microscope.

TABLE 4. SURFACE ROUGHNESS OF HEAT AGED SAMPLES

Sample	Surface roughness (μm)	
	Before heating	After heating
Untreated	0.20	0.24
Chlorinated	0.29	1.10
Brominated	0.80	0.82

Compound A. Talysurf meter cut-off 0.8 mm

Surface Roughness

For surface profile measurements, rubber samples were stuck with adhesive tape onto a glass plate and the treated surface lubricated with soapy water. Centre line average (R_a) roughness measurements were taken using 0.08 mm and 0.8 mm cut-off lengths at 5000 × vertical magnification. Charts of treated surfaces were recorded at 20× or 100× horizontal magnification. Typical results are shown in *Figure 15*. The charts were assessed visually to find values for the radius of asperities and their separation (wavelength). The typical height of asperities, their number per unit length and the R_a values are tabulated with initial friction values *(Table 6)*. The Young's modulus, E, of samples was determined using a micro-hardness gauge. The values would appear to reflect bulk rather than surface modulus *(Table 6)*. In all cases, it is apparent that treatment increased the surface roughness, to varying extents, concomitant with a fall in friction. In addition, surface hardness changes are likely to play an important role, but this factor is difficult to assess owing to a general inability to measure the surface hardness of the thin skin layer.

The following attempts to account for the fall in friction after surface treatment in terms of the induced change in surface roughness and hardness. If it is assumed that the frictional force, f, is proportional to the real area of contact, A, then

$$f = As \qquad \ldots 1$$

where s is the interfacial shear strength. For the point contact of a spherical rubber asperity on

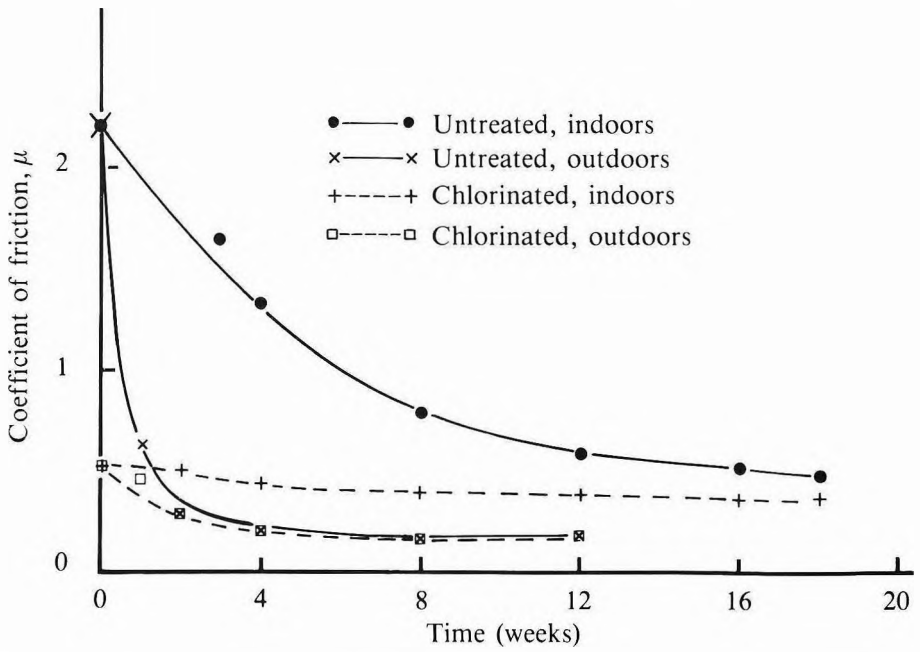


Figure 12. Sunlight exposure of surface chlorinated and untreated samples of carbon-filled NR vulcanisate (Compound A). *Carried out in UK (52°N) during spring/summer.*

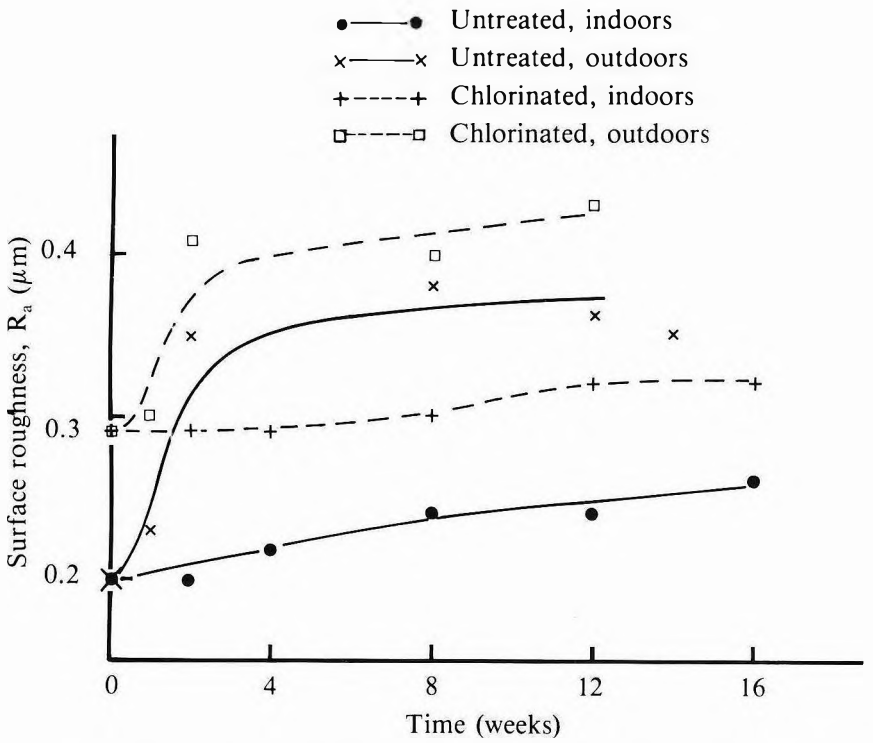


Figure 13. Change in surface roughness on sunlight exposure in UK (Compound A).

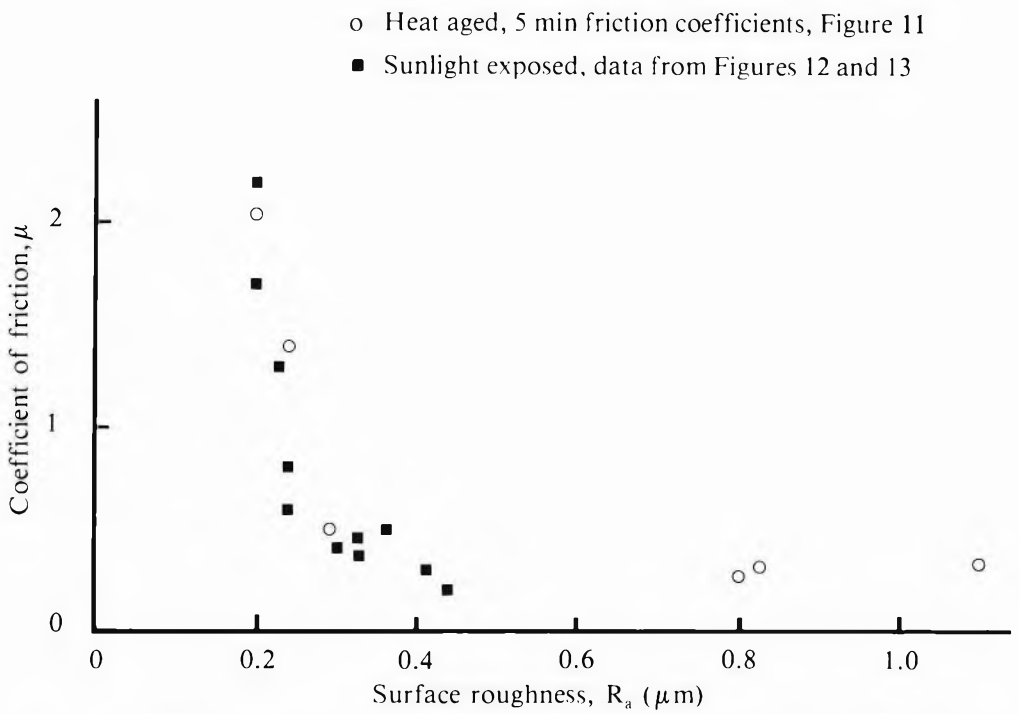


Figure 14. Friction-roughness variation for aged samples of carbon-filled NR vulcanisate (Compound A).

TABLE 5. OUTDOOR WEATHERING OF UNPROTECTED SAMPLES

Exposure time (weeks)	Friction coefficients	
	Untreated	Chlorinated
0	1.50	0.25
1	0.97	0.25
2	0.90	0.23
4	Degraded	0.21
8		0.11
16		Degraded

Compound B

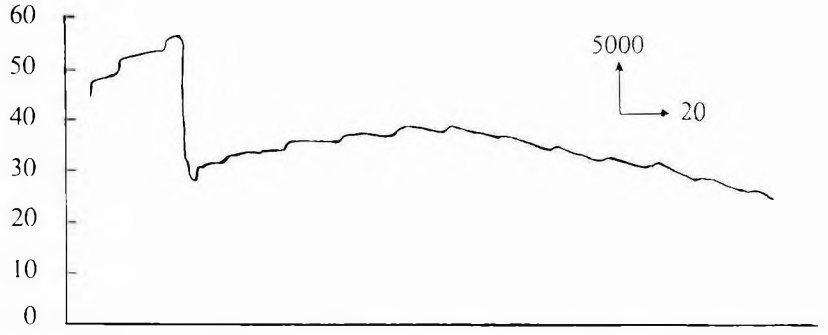
a rigid plane, *Equation 1* may be re-written to express the friction coefficient, $\mu_{asp}(=f/_w)$, related to the load, W, the sphere radius, R, and its Young's modulus, E, through the use of Hertz equation $a^3 = 9WR/16E$, where a is the radius of the circle of contact. Thus

$$\mu_{asp} = \pi s \left(\frac{9R}{16E}\right)^{2/3} W^{-1/3} \quad \ldots 2$$

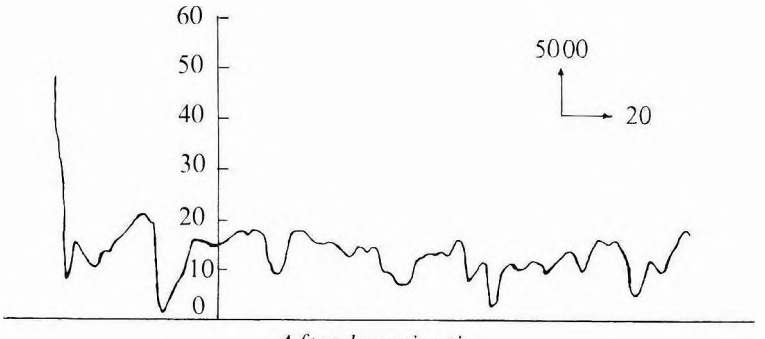
If the rubber sphere represents a single asperity on the surface of a rubber sample, then the total friction is

$$\mu = n\pi s \left(\frac{9R}{16E}\right)^{2/3} \left(\frac{P}{n}\right)^{-1/3} \quad \ldots 3$$

where n is the total number of asperities in contact and P is the total applied load to the rubber sample. This assumes all asperities are of the same radius and height. Although a considerable assumption, it brings out the general point that the friction is likely to depend on total asperity numbers and their radius. The Hertz equation applies to a semi-infinite body of uniform modulus, whereas in the present problem each asperity of modulus



Before surface treatment



After bromination

Figure 15. Surface profile charts of gum NR vulcanisate samples (Compound B) *showing before surface treatment and after bromination.*

TABLE 6. SURFACE ROUGHNESS OF TREATED RUBBER SAMPLES

Treatment	μ	E (MPa)	R (μm)	t (μm)	λ (μm)	R (μm)	n (mm^{-2})	$n^{4/3}R^{2/3}$ ($\log_{10}$)
None	1.55	0.9	0.06	0.1	100	12 500	235	6.09
				0.05	100	25 000	125	5.72
F	0.15	1.0	0.38	1.2	100	1 040	110	4.73
				1.6	100	780	85	4.49
Cl	0.50	1.0	0.29	0.4	100	3 125	380	5.76
				0.6	100	2 080	330	5.56
Br	0.32	1.1	0.36	0.8	250	9 765	125	5.45
				1.0	200	5 000	100	5.12
I	1.45	0.9	0.2	0.2	350	76 560	80	5.78
				0.2	200	25 000	100	5.59
Aqua regia	0.25	1.1	0.25	0.4	50	780	270	5.16
				1.6	150	1 760	80	4.69
Satreat	0.40	0.9	1.55	0.8	100	1 560	180	5.13
$KMnO_4$ 5% aq.	0.60	1.0	0.35	1.6	300	7 030	160	5.50
				1.2	200	4 170	230	5.56
$KMnO_4$ acidic	0.26	1.1	0.58	2.0	100	625	400	5.33
				1.0	150	2 810	100	4.96
H_2SO_4	0.56	1.15	0.2	0.3	200	16 660	225	5.94
	0.45	1.25	0.27	0.3	100	4 160	200	5.47
H_2SO_4 (25%)	1.40	1.0	0.16	0.4	125	7 880	200	5.52
HNO_3	1.44	0.95	0.24	0.2	100	6 250	200	5.60

μ = Friction coefficient; E = Young's modulus; *Compound B*

R_a = Centre line average roughness at 0.8 mm cut-off

t = Peak-to-valley height

λ = Wavelength of asperities

R = Asperity radius = $\lambda^2/8t$

n = Estimated number of asperities from Talysurf trace

E rests on a softer rubber bulk. However, with the assumption that all asperities are of the same radius and height, the error associated with applying the simple Hertz equation should not be significant.

The surface roughness results *(Table 6)* are plotted in two ways. One is as a variation of friction coefficient with the parameter $n^{4/3}R^{2/3}$ as suggested by *Equation 3*, the other is simply with R_a. The plots *(Figure 16)* indicate the importance of roughness in determining the friction level. Better account needs to be taken of asperity shape, as derived through measures of asperity height and wavelength. Quite how to handle parameter plots of high friction surfaces ($\mu > 1.4$) is not clear. Such surfaces appear (under the microscope) to form a continuous contact over extensive areas when pressed against wavy glass, whereas contact is visibly discontinuous (looks frosty) for low friction surfaces ($\mu < 0.6$). What does appear to be more certain is that surface roughness influences the level of friction, outweighing any physico-chemical interactions at the sliding interface. This is not to say that such interac-

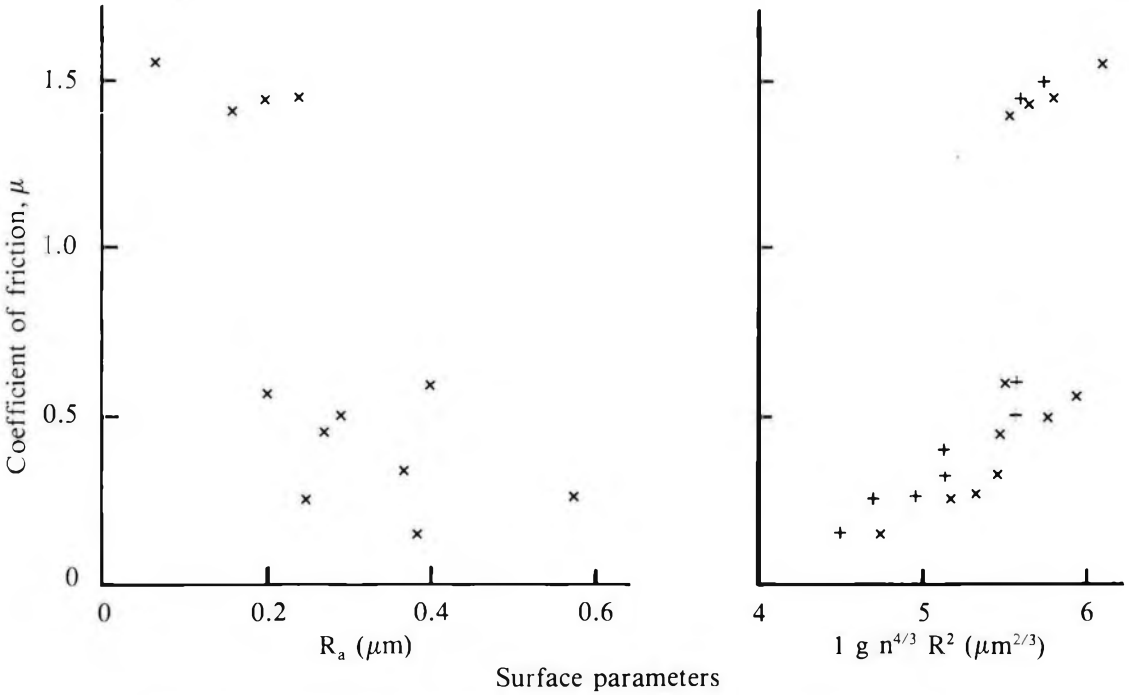


Figure 16. Variation in friction with surface roughness (Compound B).

tions do not exist, but compared to roughness they are secondary in effect.

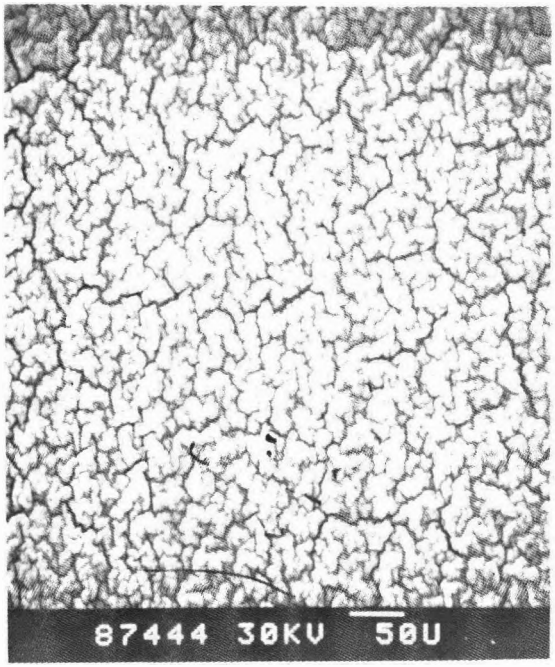
Scanning Electron Microscopy

Variously treated rubber samples were examined by SEM. The result of immersion for 4 min in saturated bromine water was a matt appearance to the sample, and SEM showed the gross nature of the bromine attack *(Figure 17)*. Electron probe micro-analysis indicated a high level of bromine chemically bonded to the rubber. There appear to be asperities upon asperities. How to relate these photographs to the Talysurf trace *(Figure 15)* of the same surface is not clear. The Talysurf diamond stylus has a square pyramid tip of side 2 μm. Presumably features on a finer scale than this will not be resolved, so the Talysurf trace represents an average of the more gross features seen in the SEM photographs.

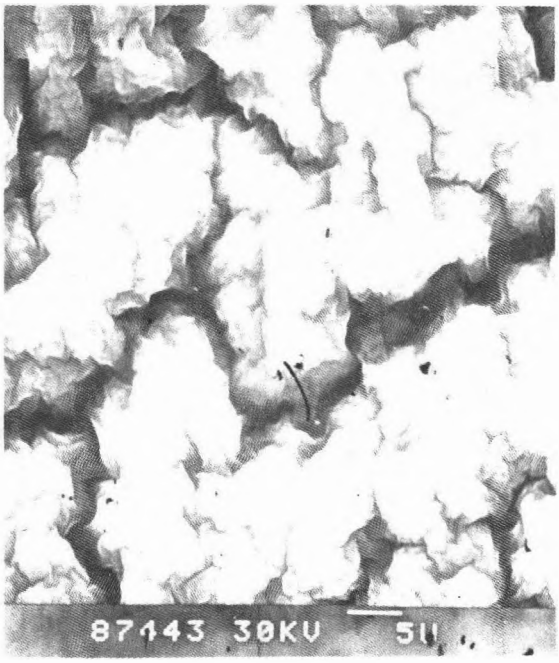
Chlorine attack by the standard method of acidified hypochlorite solution also shows surface roughening *(Figure 17)*. Mild attack (insufficient chlorine) shows only a small change in appearance *(Figure 17)* but full attack (3 min in 0.3% chlorine solution) gives considerable surface modification *(Figure 17)*. Difficulties in the manufacture of articles involving surface chlorination may be associated with insufficient chlorine in solution (old reagents), so resulting in too high a level of friction.

CONCLUSION

By using Talysurf measurements, coupled with SEM photographs, it becomes clear that chemical surface treatments produce surface roughening of a rubber sample, and this reduces the friction because the real area of contact is diminished. It is observed that different treatments produce different degrees of roughness. Thus a judicious choice of treatment could help to achieve the desired level of friction.

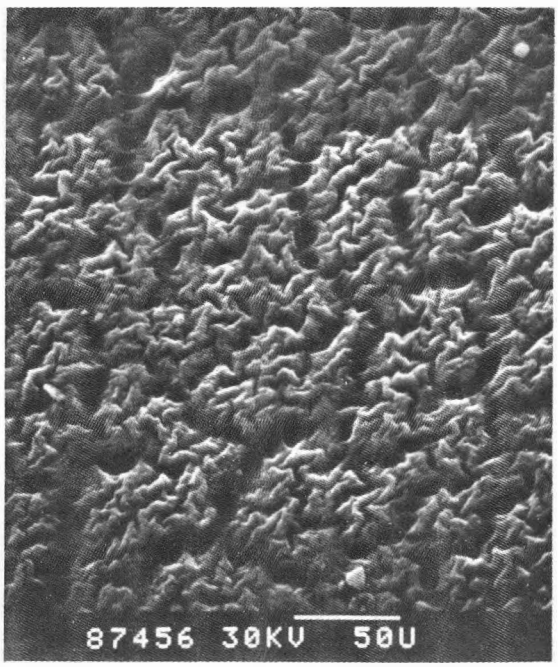


Brominated



Brominated

Mild chlorination



Full chlorination

Figure 17. Scanning electron micrographs of surface treated gum NR vulcanisate (Compound B).

ACKNOWLEDGEMENT

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REFERENCES

1. PARKES, A. (1846) Treating Caoutchouc and Gutta Percha, *Br. Pat. No. 11147.*
2. GLADSTONE, J.H. AND HIBBERT, W. (1888) The Optical and Chemical Properties of Caoutchouc. *J. Chem. Soc.,* **53,** 679.
3. LEE, D.F., SCANLON, J. AND WATSON, W.F. (1963) The Cyclization of Natural Rubber. *Proc. R. Soc.,* **A273,** 345.
4. NAUNTON, W.J.S. (1961) *The Applied Science of Rubber.* London: Edward Arnold.
5. ROFF, W.J. AND SCOTT, J.R. (1971) *Fibres, Films, Plastics and Rubbers.* London: Butterworths.
6. STERN, H.J. (1967) *Rubber: Natural and Synthetic.* London: Butterworths.
7. WEBER, L.E. (1926) *Chemistry of Rubber Manufacture.* London: Griffin.
8. USSR PATENT (1983) Volzhskii Plant of Rubber Technical Articles. Surface Modification of Industrial Rubber Products. *SU 1002312.*
9. POLITECHNIKA LODZKA: INSTITUTE PRZEMYZLY GUMOWEGO (1980) Superficial Resistant Film on Rubber Products. *Pol. Pat. 105791*
10. PAUTRAT, R., METIVIER, B. AND MARTEAU, J. (1975) Changes Occurring in Natural Rubber Through the Action of Chlorosulphonyl Isocyanate. *Proc. Int. Rubb. Conf. 1975 Kuala Lumpur,* **4,** 267.
11. DUNLOP LTD (1941) Improvements in Treating Surfaces of or containing Rubber or the Like. *Br. Pat. No. 535 983.*
12. VITEK INC; MARCHEM INC. (1978) Method of Treating Extensible Hydrocarbon Articles. *Br. Pat. No. 1522395.*
13. ANATOLIEVICH, E. (1981) Manufacturing Surface Modified Rubber Articles. *U.K. Pat. Applic. No. 2062649A.*
14. NUDELMAN, Z.N. AND PROKUDIN, I.P. (1974) Process for Surface Fluorination of Rubber Articles. *Br. Pat. 1378485.*
15. CHESNOKOV, N.M., SEMENOV, I.V., YABLONSKI, N.S. AND PAL'MOVA, N.I. (1979) Seal Rubbers with Antifriction Coatings. *Kauchuk i Rezina,* **7,** 42.
16. DOEDE, C.M. (1961) Slippery Rubber. *Rubb. Age,* **89,** 110.
17. ORLOV, V.A. AND ROSTOVTSEVA, E.E. (1975) Surface Bromination of NR Vulcanizates for Improvement in Performance Characteristic. *Proc. Int. Rubb. Conf. 1975 Kuala Lumpur,* **4,** 263.
18. RADNOTI, A., SERA, J., SCHOBER, M. AND FEDENYI, G. (1978) Surface Treatment of Rubber with Bromine. *Huanyages Gummi,* **15,** 363.
19. FOOD MACHINERY AND CHEMICAL CORP. (1961) Peracetic Acid Treatment of Vulcanized Rubber. *Br. Pat. No. 861 660.*
20. POHR, H.C., RYCK, F.M., WALLIS, C.T. (1960) Squeegee. General Motors *U.S. Pat. No. 2952865.*
21. RUNTON, L.A. AND MORTON, H.C. (1959) Russell Mfg Co. *U.S. Pat. No. 2908028.*
22. SYMBOLIK, W.S. (1963) Squeegee Type Wiper Blade. General Motors. *U.S. Pat. No. 3080596.*
23. SLADE, R.W. (1969) Method for Surface Modification of Elastomer and Windshield Wiper Produced by Same. Ford Motor Co. Ltd. *Br. Pat. No. 1147577.*
24. RUSCH, K.C. AND FORRESTER, J.R. (1971) Frictional Characteristics of EPDM Windshield Wiper Blades. *Rubb. Wld,* **165,** 54.
25. GORELIK, R.A. (1980) Modification of the Surfaces of Rubber Articles. *French Pat. No. 2465761.*
26. SUTURES INC. (1975) Improvements in or Relating to Rubber Articles Having Improved Slip Coating. *Br. Pat. No. 1398552.*
27. INCO EUROPE LTD (1976) Chromium Plating of Polyolefin Compositions. *Br. Pat. No. 1534638.*
28. MILLER, B. (1978) Sputtered Chrome New Route to Plated Elastomers. *Plast. Wld,* **36,** 56.
29. DAI-ICHI KOGYO SEIYAKU CO. LTD (1974) Adhesion Prevention of Rubber to a Contiguous Surface. *Br. Pat. No. 1524721.*
30. DUKHOVSKII, E.A., KLEIMAN, A.M., PONOMAREV, A.N., SILIN, A.A., STEPANOV, B.M., TAL'ROZE, V.L., TIKHOMIROV, L.A. AND KHOMYAKOV, A.V. (1984) Surface Modification of Rubber Articles. *USSR Pat. SU 642950.*
31. YASUDA, H.K. (1984) Modification of Polymer Surfaces by Plasma Treatment and Plasma Polymerisation. *187th ACS Meet, St. Louis, Symp. on Polym. Wear and Its Control,* Ser. 287, 89.
32. ROBERTS, A.D. AND TABOR, D. (1971) Extrusion of Liquids between Highly Elastic Solids. *Proc. R. Soc.,* **A325,** 323.
33. ROMBERG, V.S. (1986) Aqueous Chlorination of NR Surfaces. *ACS (Rubb. Div.) Meet.,* Spring paper.

34. ONG, E.L. AND ROBERTS, A.D. (1986) Experiments on Lubrication of Raw NR. *J. nat. Rubb. Res.*, **1(1)**, 41.

35. TIGER POLYMER, K.K. (1981) Prevention of Adhesion of Vulcanized Rubber Sheets. *Japanese Pat. 81120328.*

36. BRIDGESTONE TIRE AND RUBBER CO. (1975) Preventing Adhesion between Substrates. *U.S. Pat. No. 3990990.*

37. DEAN, W.R., PERERA, V. AND GLAZER, J. (1958) Monulayer Studies of Some Hydroxylated Polyolefin Rubbers. *J. Polym. Sci.*, **27**, 489.

38. SATREAT (Registered Trade Mark for a Process of Chlorination Using an Organic Chlorine Containing Substance). *Br. Pat. No. 1278258, 1295676, 1295677.*

39. BARQUINS, M. AND ROBERTS, A.D. (1986) Rubber Friction Variation with Rate and Temperature: Some New Observations. *J. Phys. D: Appl. Phys.*, **19**, 547.

J. nat. Rubb. Res., **4(1)**, 22–40

A New Comparison of Sheet and Crumb Rubber. Part II. Some Aspects of Processing

G.M. BRISTOW* AND A.G. SEARS*

Complementary samples of RSS CV and crumb SMR CV covering the Mooney viscosity range ca. *50–85 were prepared from five lots of monoclonal latex. Similar processability and curing behaviour were observed for typical tread stocks prepared from these materials. Only in the case of the initial formation of bound rubber or carbon gel, a parameter indicative of rubber/black interaction, was there evidence of an obvious effect of raw rubber production procedure, but even here, this difference was eliminated in the inevitable further working during final mixing.*

In a previous paper[1], a comparison was presented of various raw rubber properties of samples of monoclonal SMR CV (crumb) and RSS CV (sheet). Here, data characterising some aspects of processing behaviour for these samples are considered. The main theme is a comparison between the sheet and crumb materials derived from a common (monoclonal) latex source. The processing qualities considered are:

- Susceptibility to oxidative or mechano-chemical breakdown
- Banbury mixing of fine particle size carbon black (N220, ISAF black) in a typical tread stock
- Capillary extrusion behaviour of materials prepared by Banbury mixing of fine particle size carbon black.

EXPERIMENTAL

Breakdown Properties

Breakdown was assessed in three different ways: by the well-established PRI test, by mastication in a Brabender plasticorder[2] (Model PLV 151) and by the hot pressing test described by Lim and Lim[3]. In each case, rubber blended according to the SMR procedure[4] was used.

The plasticorder was equipped with an N50H mixing chamber, cam-type rotors and a standard pressure ram. The machine was heated by circulating oil to either 60°C or 100°C, after which 60 g of rubber, corresponding to a fill factor of 0.82, was masticated at 100 r.p.m. for 4 min. At the end of this period, at which time the rubber temperature as indicated by the built-in thermocouple probe was 100°C–115°C or 130°C–145°C depending on the machine temperature, the rubber was rapidly removed and cooled by a single pass through a cold two-roll mill. Mooney viscosity, V_R *mast.* (ML1 + 4, 100°C) was measured after a resting period of 18–24 h. Breakdown was expressed either as the simple decrease in viscosity, ΔV_R, or by a breakdown index, BI, where:

$$\text{BI} = \frac{\Delta V_R \, 10^4}{\text{Initial } V_R \, Wu}$$

Wu being the total work per unit volume (MJ/m^3), obtained from integration of machine torque as a function of time[5]. Typical within-blend reproducibility, separately determined from five replicate tests on a single sample of blended SMR L, was:

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	Mean	S.D.	C.V. (%)
V_R *mast.*	77.9	0.4	0.5
BI	1.25	0.05	3.7
Dump temperature (°C)	151.0	0.7	0.5

The hot pressing test was operated in the manner indicated by Lim and Lim[3] using a platen temperature of 200°C and a sample thickness of 0.5 mm. Breakdown was expressed as ΔV_R or $VRP = (\Delta V_R/\text{Initial } V_R) \times 10$.

Typical within-blend reproducibility, separately determined from ten replicate tests on a single sample of blended SMR CV, was:

	Mean	S.D.	C.V. (%)
V_R *pressed*	48.5	0.47	0.97
VRP	2.42	0.08	3.12

Banbury Mixing

The masterbatch formulation shown in *Table 1* was mixed in a BR Banbury at a batch factor of 8 and under the following conditions:

Masterbatch mixing cycle

0 min : Add rubber
1 min : Add small powders, black and oil
2 min : Sweep
3 min : Discharge
Cool by one pass through cool two-roll mill

Remill cycle

0 min : Add masterbatch
2 min : Discharge
Cool by one pass through cool two-roll mill

BR Banbury rotor speed 155 r.p.m., starting temperature 50°C–60°C, cooling water 7.6 litres/min

Weight losses during mixing were *ca.* 0.5%. The mixing operation was characterised in terms of gross energy and dump temperature. The power-time traces gave no real indication of black incorporation time (BIT), consistent with previous experience in these laboratories of mixing practical 100% NR stocks in this type of mixer. While BIT phenomena may be readily apparent in the BR Banbury with some synthetic rubbers, they are only obvious with NR at high levels of black and preferably in the absence of plasticiser and zinc soaps[6].

TABLE 1. FORMULATION FOR TEST COMPOUNDS

Item	Parts by weight
Masterbatch	
Natural rubber, unmasticated	100
N220, ISAF black	45
Process oil[a]	5
Zinc oxide	5
Stearic acid	3
IPPD[b]	2
Curatives[c]	
Sulphur	2.5
TBBS[d]	0.5

[a] Aromatic process oil, Dutrex 729 HP (Shell Chemicals)

[b] N-Isopropyl-N′-phenyl-*p*-phenylenediamine, Permanax IPPD (Vulnax International)

[c] Added on a two-roll mill after resting for a further 24 h

[d] N-*t*-Butylbenzothiazole-2-sulphenamide, Santocure NS (Monsanto)

The mixes (masterbatches) were characterised by values of Mooney viscosity, V_B, Cabot dispersion rating[7] and bound rubber after 48 h immersion in toluene. In order to avoid testing final mixes of atypically high viscosity, after 24 h the masterbatches from the highest viscosity clones RRIM 628 and PR 261 were remilled for 2 min in the Banbury under the same conditions as before. After resting for a further 24 h, curatives *(Table 1)* were added on a two-roll mill. Tests on these final mixes comprised viscosity, V_c, bound rubber content and rheometry at 150°C.

Capillary Flow Tests

An Instron 3211 rheometer was used with two capillaries, both 1.27 mm in diameter but

having different lengths: 2.54 mm and 25.4 mm. Testing was limited to two piston speeds corresponding to Newtonian shear rates of *ca.* 95 s^{-1} and 445 s^{-1}. Values for wall shear stress π_w, end correction *e,* flow index *n,* and extrudate area swell were derived as described previously[1].

RESULTS AND DISCUSSION

The presentation of the test data is the same as that adopted in *Part I*[1]. That is, results are presented where appropriate as overall mean and standard deviations for the sheet and crumb materials and, more importantly, as values of the difference (sheet minus crumb) for the five clones, together with means and standard deviations for these differences.

Data characterising raw rubber breakdown are given in *Table 2* and further analysed in *Table 3*. Rather surprisingly, perhaps, the sheet materials show slightly lower values of PRI than the crumb rubbers and, consistent with this, mean values of ΔV_R in the Brabender and 200°C pressing tests are larger for the sheet than the crumb rubbers. No such correlation exists, however, for the individual materials. Some discrepancy is evident here with the results of Lim and Ong[8], who found that, in the Brabender test, value of ΔV_R for samples of standard, unstabilised RSS 1 were much *lower* than those for a range of SMR crumb grades including SMR CV. The obvious interpretation of this apparent conflict is that the hydroxylamine neutral sulphate treatment used to prepare RSS CV has destroyed, or offset, this unique character of RSS 1. It must be noted, however, that Lim and Ong's values for SMR L were not greatly different from those they obtained for SMR CV. Furthermore, very limited studies of monoclonal SMR L and SMR CV in these laboratories have given *lower* ΔV_R values for the CV materials[9].

Despite the limited consistency between low PRI and high ΔV_R for the Brabender and pressing tests noted above, correlations between the three breakdown parameters are very poor. This is shown by the coefficients recorded in *Table 4* and is very evident in the plots of *Figures 1, 2* and *3*. For the Brabender, breakdown at both 60°C and, especially, 100°C correlates quite well with the *initial* viscosity of the rubber *(Figure 4)*. As shown by the excellent correlations of *Figure 5,* greater breakdown stems from the higher heat generation achieved with a higher viscosity rubber. Finally, and most importantly in the present context, in all these correlations, good and bad, there is no evidence for specific effects of the sheet or crumb nature of the rubber.

Data for the mixing of the tread stock from unmasticated rubber are given in *Table 5* with further analysis in *Table 6*. The mixing process was characterised by two parameters, mixing energy and dump temperature. The results show that neither of these discriminates between sheet and crumb rubbers. Furthermore, and rather unexpectedly, neither shows any dependence on the initial viscosity of the rubber.

In keeping with the trends noted for raw rubber breakdown, viscosity of the masterbatch is, as shown in *Figure 6,* strongly dependent on that of the raw rubber and the same regression equation:

$$V_B = 8.76 + 1.07\ V_R$$

Correlation coefficient = 0.995

fits both the SMR CV and RSS CV materials. The black dispersion rating of the masterbatch also shows a (negative) correlation with rubber viscosity but here there is slight evidence that inferior dispersion is attained with the sheet rubbers *(Figure 7)*. At the final mix stage, viscosity still shows a correlation with raw rubber viscosity though, as shown in *Figure 8,* the dependence is less marked:

$$V_C = 28.97 + 0.347\ V_R$$

Correlation coefficient = 0.905

No differences in black dispersion were evident after final mixing.

While, despite extensive measurements over many years, the technological significance of bound rubber (carbon gel) remains obscure, in the present instance such measurements do in fact differentiate between sheet and crumb, at least at the masterbatch stage. This is clearly apparent in the plots of percent bound rubber

TABLE 2. RAW RUBBER BREAKDOWN PARAMETERS

Item	SMR CV					RSS CV				
	RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261	RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261
PRI	91	90	81	83	88	89	81	75	78	85
ML1+4, 100°C V_R	52.5	56.5	84	52	67.5	57	62	87	56	72.5
Brabender mastication 4 min at 100 r.p.m.										
Machine temperature, 60°C										
Final temperature (°C)	101	104	114	102	108	102	106	116	103	110
V_R mast.	45	50	76	46	58.5	48	55	78	49	62
ΔV_R	7.5	6.5	8	6	9	9	7	9	7	10.5
BI	1.71	1.33	0.94	1.38	1.43	1.83	1.22	1.36	1.50	1.49
Machine temperature, 100°C										
Final temperature (°C)	131	134	145	130	137	134	137	147	134	141
V_R mast.	46.5	52	76	46.5	59	49	54	76	49	61
ΔV_R	6	4.5	8	5.5	8.5	8	8	11	7	10.5
BI	1.47	0.99	0.99	1.46	1.46	1.78	1.48	0.28	1.56	1.78
200°C pressing test										
V_R after pressing	41	46	80	39	56	43	48	81	40	58
ΔV_R	11.5	10.5	4	13	11.5	14	14	6	16	14.5
VRP	2.19	1.86	0.48	2.50	1.70	2.46	2.26	0.69	2.86	2.00

TABLE 3. FURTHER ANALYSIS OF THE DATA OF *TABLE 3*

Item	RSS CV		SMR CV		Δ (RSS CV - SMR CV)						
	Mean	S.D.	Mean	S.D.	RRIM 600	RRIM 623	RRIM 628	RRIM 700	PR 261	Mean	S.D.
PRI	81.6	5.6	86.6	4.4	−2	−9	−6	−5	−3	−5.0	2.7
Brabender mastication											
Machine temperature, 60°C											
Final temperature (°C)	107.4	5.7	105.8	5.3	+1	+2	+2	+1	+2	+1.6	0.5
ΔV_R	8.5	1.5	7.4	1.2	+1.5	+0.5	+1	+1	+1.5	+1.1	0.4
Machine temperature, 100°C											
Final temperature (°C)	138.6	5.5	135.4	6.0	+3	+3	+2	+4	+4	+3.2	0.8
ΔV_R	8.9	1.7	6.5	1.7	+2	+3.5	+3	+1.5	+2	+2.4	0.8
200°C pressing test											
ΔV_R	12.9	3.9	10.1	3.5	+2.5	+3.5	+2	+3	+3	+2.8	0.6

TABLE 4. CORRELATIONS BETWEEN VARIOUS BREAKDOWN PARAMETERS

Parameter	Data points	Correlation coefficient	Significance (%)
ΔV_R Brabender, PRI			
60°C	10	0.015	< 90
100°C	10	−0.489	< 90
ΔV_R Brabender, ΔV_R 200°C pressing			
60°C	10	−0.079	< 90
100°C	10	−0.386	< 90
Plasticity Retention Index, ΔV_R 200°C pressing	10	0.245	< 90
ΔV_R Brabender, initial V_R			
60°C	10	0.573	90–95
100°C	10	0.769	99
Final Brabender temperature, ML1 + 4, 100°C			
60°C	10	0.992	> 99.9
100°C	10	0.988	> 99.9

versus V_B and bound rubber swelling *versus* V_B of *Figures 9* and *10* respectively. As might be anticipated, the discrimination between sheet and crumb is no longer evident if percent bound rubber is plotted against bound rubber swelling *(Figure 11).* Conversion of masterbatch to final mix (*via* a remill stage for clones RRIM 628 and PR 261) results in a decrease in bound rubber *(Figure 12)* together with an increase in swelling *(Figure 13)* and, more importantly, the disappearance of any consistent difference between sheet and crumb.

The obvious interpretation of these results is that, while initially during the preparation of masterbatch the interaction between carbon black and rubber is greater for RSS, this is levelled out during subsequent reworking and/or preparation of the final mix. The last measure used to characterise the final mixes, rheometric cure behaviour, also shows no difference between batches based on sheet and crumb and will be considered again in *Part III.*

On the basis of the above results, no differences in downstream processability would be expected between sheet and crumb-based materials. Further confirmation of such parity has been sought in capillary extrusion performance at modest (95 s^{-1}) and high (445 s^{-1}) shear rates. The results in terms of wall shear stress, flow index, and correction and extrudate swell, derived as indicated in *Part I*[1] are given in *Tables 7* and *8.*

In the first place it is to be noted that, as shown in *Figure 14,* good correlations exist between the Mooney viscosity, V_c, and wall shear stress at both low and high shear rates. However, the 'normalised' slopes:

$$\text{Slope} \quad \frac{\text{Mean } V_c}{\text{Mean } \pi_w}$$

of the regression lines, together with the likely relative precision of the measured values of π_w and V_c, suggest that Mooney viscosity will

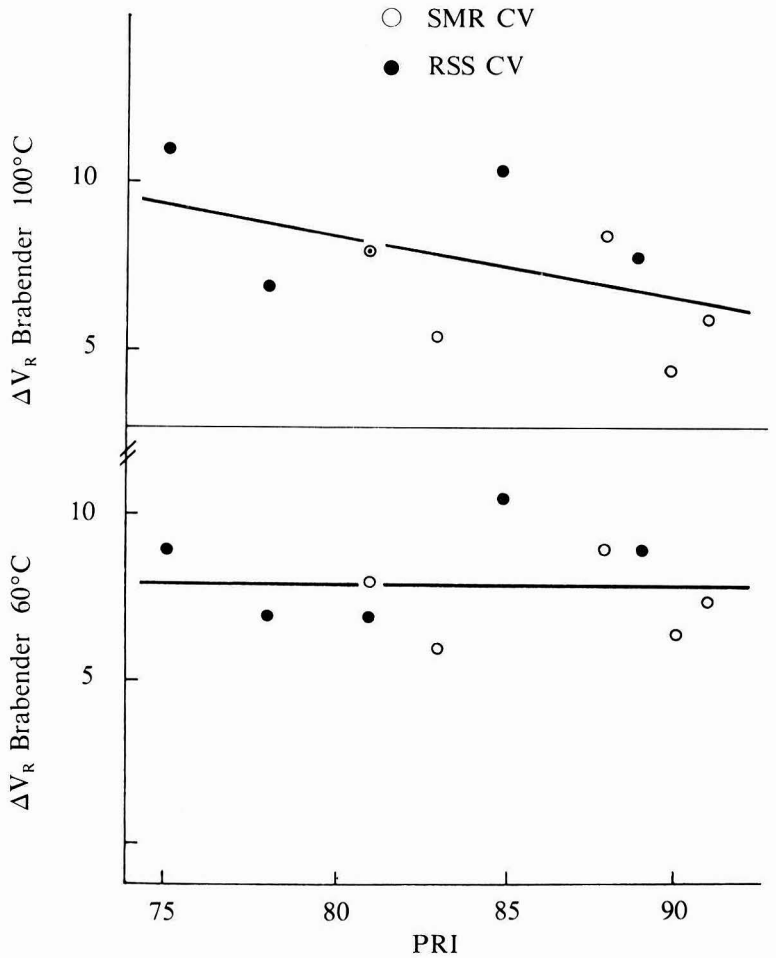

Figure 1. Correlation of Brabender breakdown and PRI.

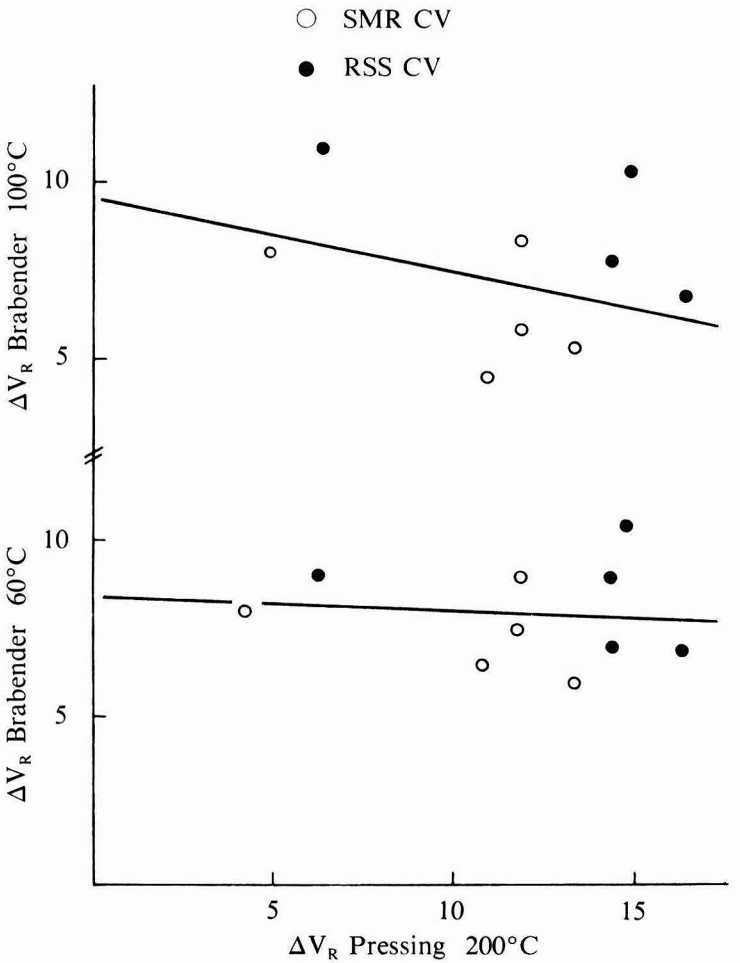

Figure 2. Correlation of Brabender breakdown and breakdown in pressing at 200°C.

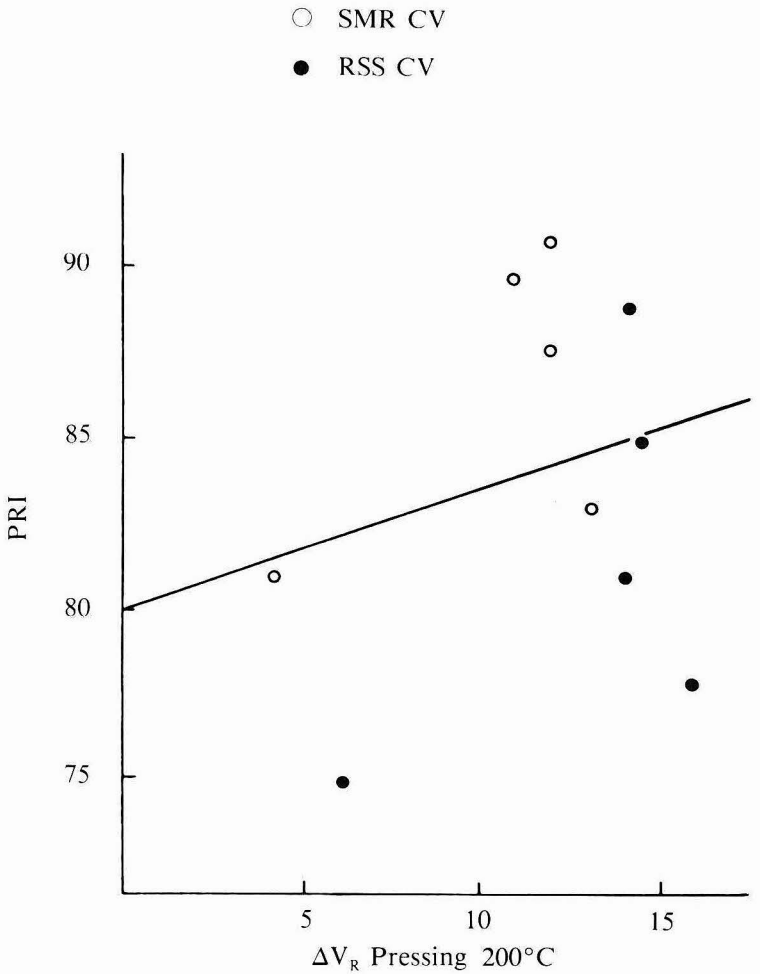

Figure 3. Correlation of PRI and breakdown in pressing at 200°C.

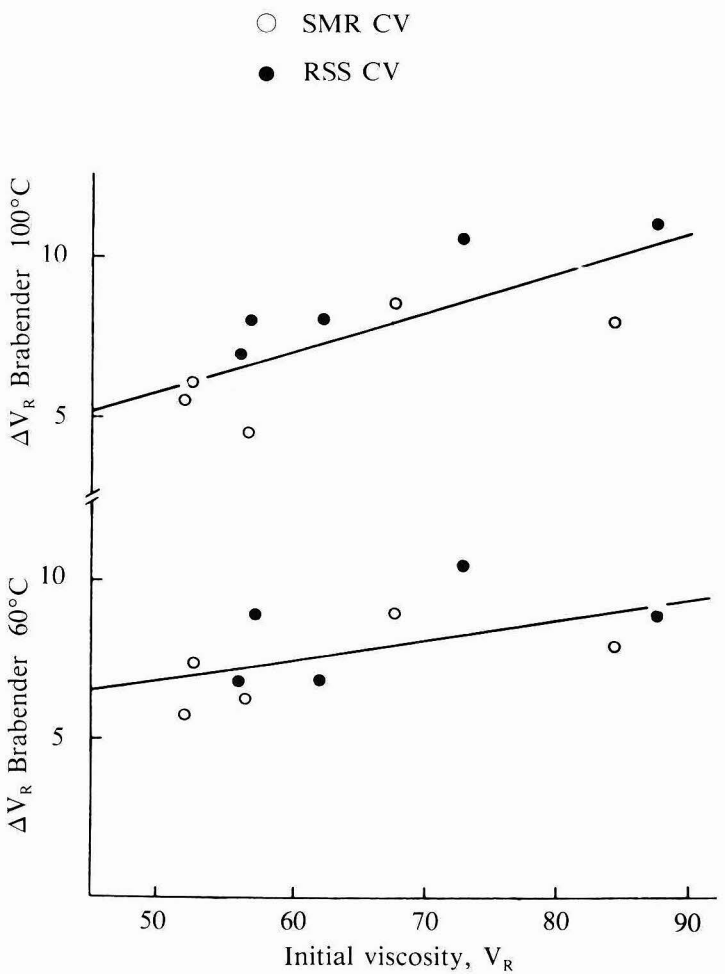

Figure 4. Dependence of Brabender breakdown on initial rubber viscosity.

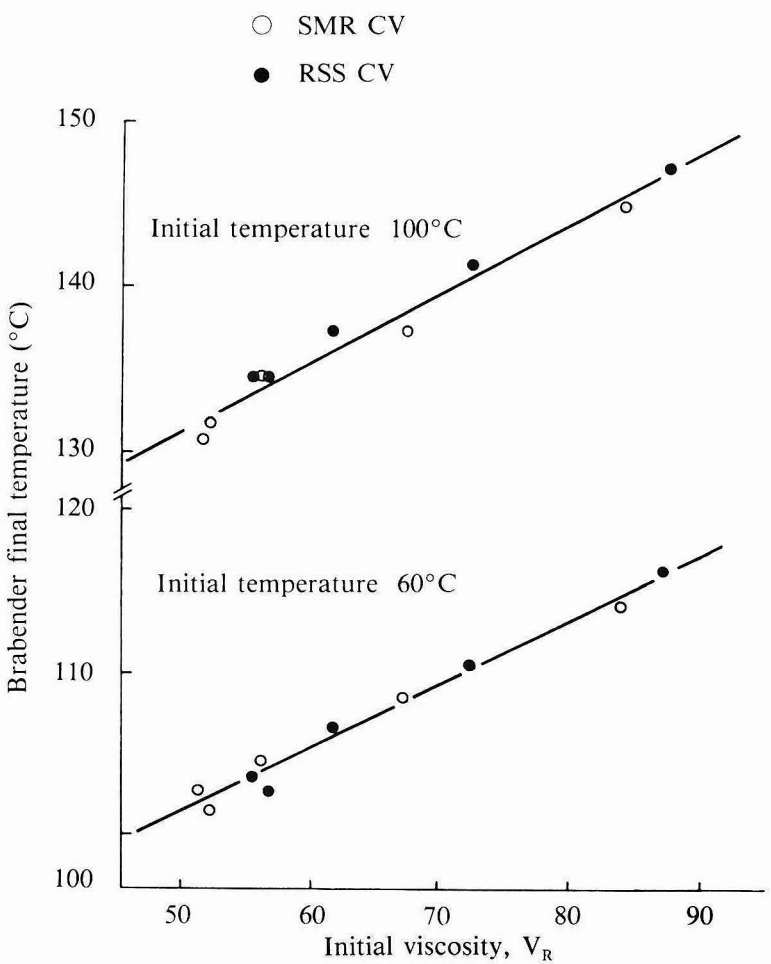

Figure 5. Dependence of Brabender dump temperature on initial rubber viscosity.

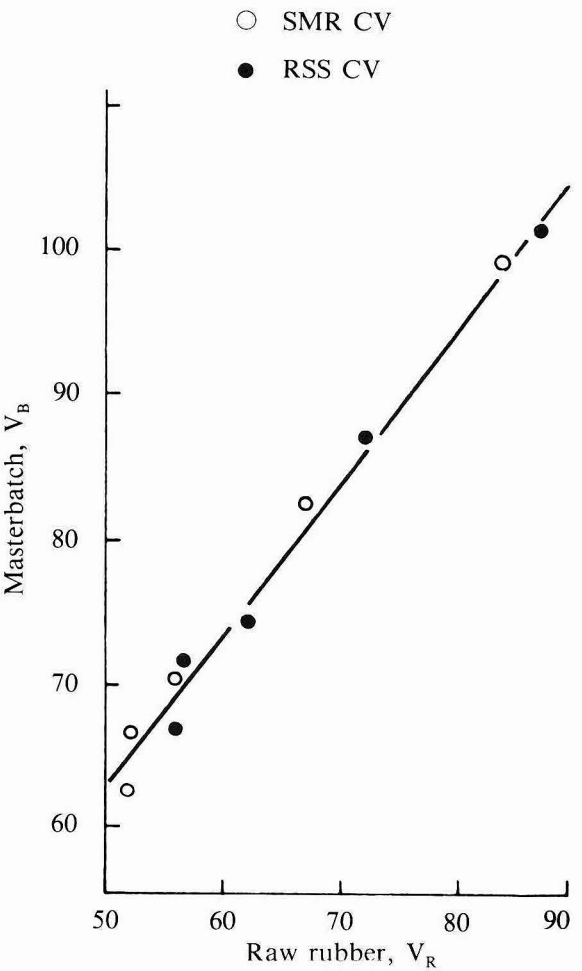

Figure 6. Dependence of tread masterbatch viscosity on raw rubber viscosity.

TABLE 5. BANBURY MIXING OF TREAD COMPOUND

Parameter	SMR CV					RSS CV				
	RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261	RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261
Masterbatch										
ML1+4, 100°C, V_B	66.5	70.5	99	62.5	82.5	71.5	74.5	101.5	67	87
Gross energy (MJ/m^3)	1 870	1 730	1 730	1 560	1 730	1 580	1 680	1 730	1 630	1 730
Dump temperature (°C)	129	130	128	127	133	128	130	132	128	133
Cabot black dispersion[a]	C1-3	B1-3	D1-3	C1-3	C1-3	D1-3	C1-3	E1-3	C1-3	D1-3
Bound rubber wt (%)	44.2	45.8	58.3	42.4	50.5	50.8	51.2	62.5	50.2	57.9
Bound rubber swell (wt/wt)[b]	33.9	35.9	29.6	37.2	32.4	30.5	32.7	26.3	33.3	28.6
V_B-V_R	14	14	15	10.5	15	14.5	12.5	14.5	11	14.5
Remill										
ML1+4, 100°C, V_{BR}	—	—	75	—	66	—	79	—	—	71
Gross energy (MJ/m^3)	—	—	1 060	—	960	—	1 030	—	—	1 060
Dump temperature (°C)	—	—	125	—	133	—	130	—	—	125
Cabot black dispersion	—	—	A1	—	A2	—	A2	—	—	A2
Bound rubber wt (%)	—	—	39.2	—	38.6	—	45.3	—	—	37.5
Bound rubber swell (wt/wt)	—	—	39.2	—	42.8	—	36.3	—	—	42.9
V_{BR}-V_R	—	—	−9	—	−1.5	—	−8	—	—	−1.5
Final mix										
ML1+4, 100°C, V	48.5	45	56.5	46	52	47	52	59	51	57
Bound rubber wt (%)	30.6	28.8	35.1	30.3	35.8	33.1	35.4	35.5	33.0	37.0
Bound rubber swell (wt/wt)	51.0	49.3	51.1	52.6	50.2	42.2	41.1	47.1	46.0	50.0
V_c-V_R	−4	−11.5	−27.5	−6	−15.5	−10	−10	−28	−5	−15.5
Monsanto rheometer, 150°C, 1° arc										
M_{HR} — M_L(torque units)[c]	28.3	29.4	28.5	27.7	26.7	28.9	29.3	28.6	27.4	27.4
Scorch time, t_{s1} (min)	4.3	3.9	3.9	4.2	4.6	3.2[d]	3.7	4.2	4.0	4.6
Cure time, t_c' (90) (min)	14.2	14.0	14.7	15.1	15.7	12.9[d]	14.0	15.0	14.3	15.3
Cure time, t_c' (95) (min)	16.3	16.3	17.1	17.5	18.1	15.1[d]	16.4	17.4	16.6	17.6
t_{RI}[e]	34.5	34.0	36.0	36.5	38.0	33.0	36.0	37.5	35.5	38.0

[a] Proportion of undispersed black: A (low) — H (high), particle size: 1 (small) — 6 (large)

[b] Weight solvent/weight bound rubber

[c] 1 torque unit = 0.11 Nm

[d] Omitted from analysis of *Table 6*

[e] Time to 0.11 Nm reversion (min)

TABLE 6. FURTHER ANALYSIS OF THE DATA OF *TABLE 5*

Parameter	RSS CV		SMR CV		Δ (RSS CV – SMR CV)						
	Mean	S.D.	Mean	S.D.	RRIM 600	RRIM 623	RRIM 628	RRIM 700	PR 261	Mean	S.D.
Masterbatch											
Gross energy (MJ/m^3)	1 670	65	1 720	110	−290	−50	0	+70	0	—	—
Dump temperature (°C)	130	2	129	2	−1	0	+4	+1	0	1	2
ML1+4, 100°C, V_B	—	—	—	—	+5	+4	+2.5	+4.5	+5.5	+4.3	1.2
V_B–V_R	13.4	1.6	13.9	1.9	+0.5	−1.5	−0.5	+0.5	−0.5	−0.3	0.8
Bound rubber wt (%)	54.5	5.4	48.2	6.4	+6.6	+5.4	+4.2	+7.8	+7.4	+6.3	1.5
Bound rubber swell (wt/wt)	30.3	2.9	33.8	3.0	−3.4	−3.2	−3.3	−3.9	−3.8	−3.5	0.3
Final mix											
ML1+4, 100°C, V_C	53.2	4.8	49.6	4.7	−1.5	+7	+2.5	+5	+5	+3.6	3.3
$V_C - V_R$	−13.7	8.8	−12.9	9.3	−6	+1.5	−0.5	+1	0	−0.8	3.0
Bound rubber wt (%)	34.8	1.7	32.1	3.1	+2.5	+6.6	+0.4	+2.7	+1.2	+2.7	2.4
Bound rubber swell (wt/wt)	45.3	3.6	50.8	1.2	−8.8	8.2	−4.0	−6.6	−0.2	−5.6	3.5
Monsanto rheometer, 150°C, 1° arc											
$M_{HR} - M_L$ (torque units)	28.3	0.9	28.1	1.0	0.6	−0.1	0.1	−0.3	0.7	0.2	0.4
Scorch time, t_{s1} (min)	3.9	0.5	4.2	0.3	−1.1[a]	−0.2	0.3	−0.2	0	0	0.2
Cure time, t_c' (90) (min)	14.7	0.6	14.7	0.7	—	0	0.3	−0.8	−0.4	−0.2	0.5
Cure time, t_c' (95) (min)	17.0	0.6	17.1	0.8	—	0.1	0.3	−0.9	−0.5	−0.3	0.6
t_{RI}	36.0	2.0	35.8	1.6	−1.5	2	1.5	−1	0	0.2	1.5

[a] Omitted from analysis of *Table 5*

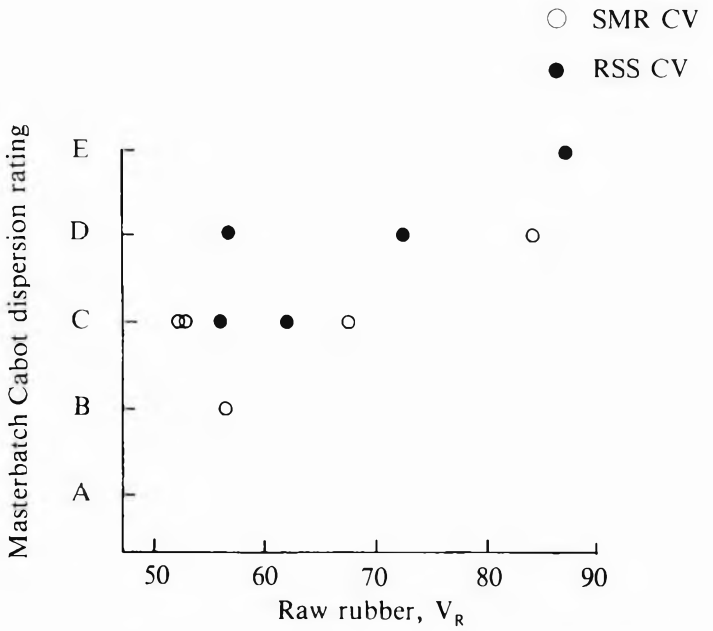

Figure 7. Dependence of masterbatch Cabot dispersion rating on raw rubber viscosity.

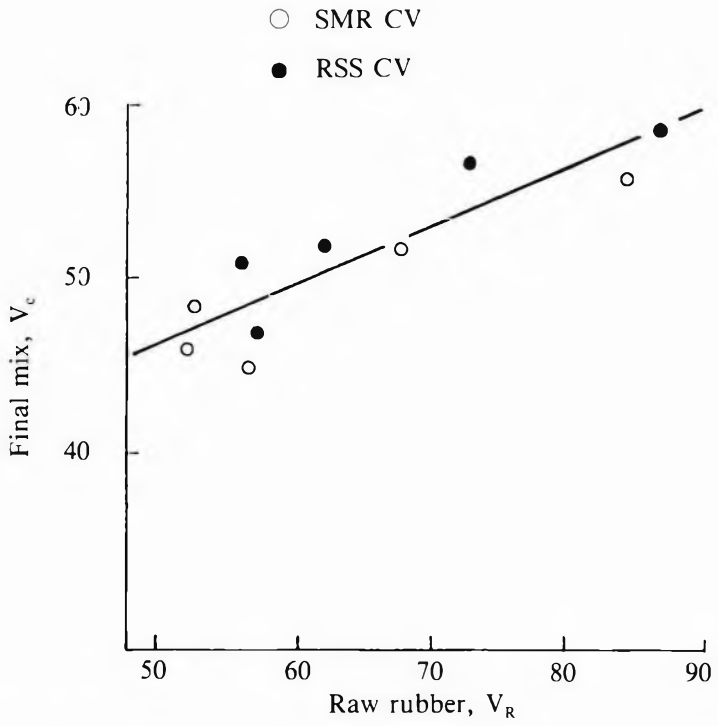

Figure 8. Dependence of final mix viscosity on raw rubber viscosity.

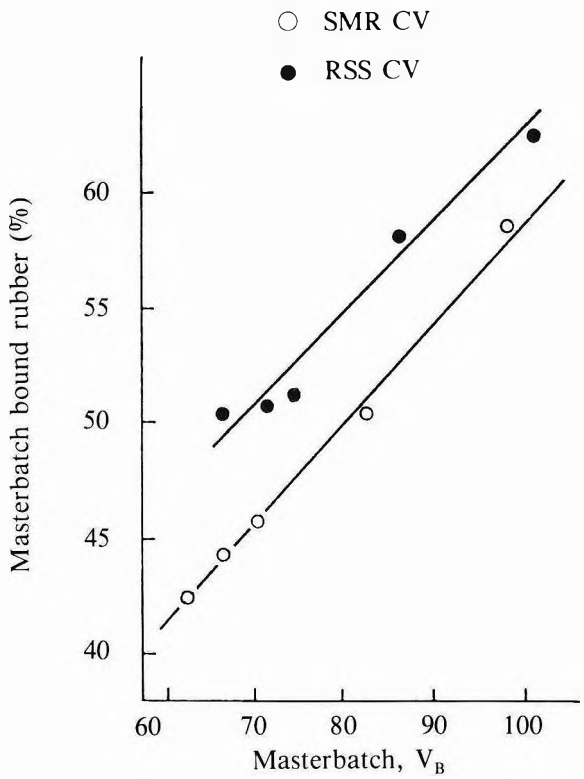

Figure 9. Dependence of masterbatch bound rubber on masterbatch viscosity.

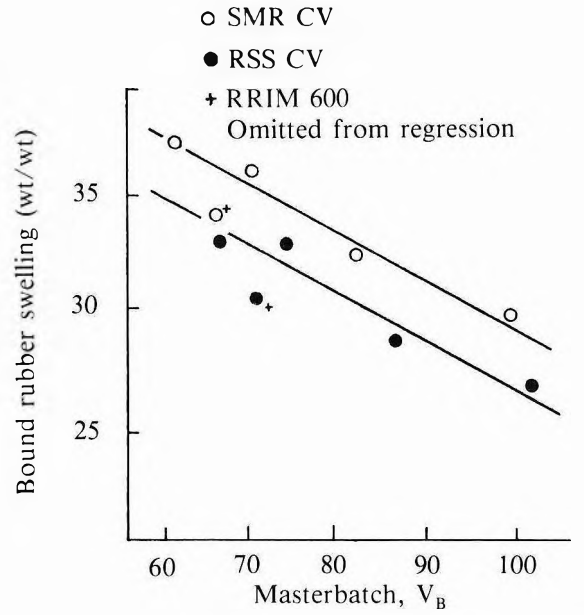

Figure 10. Dependence of bound rubber swelling on masterbatch viscosity.

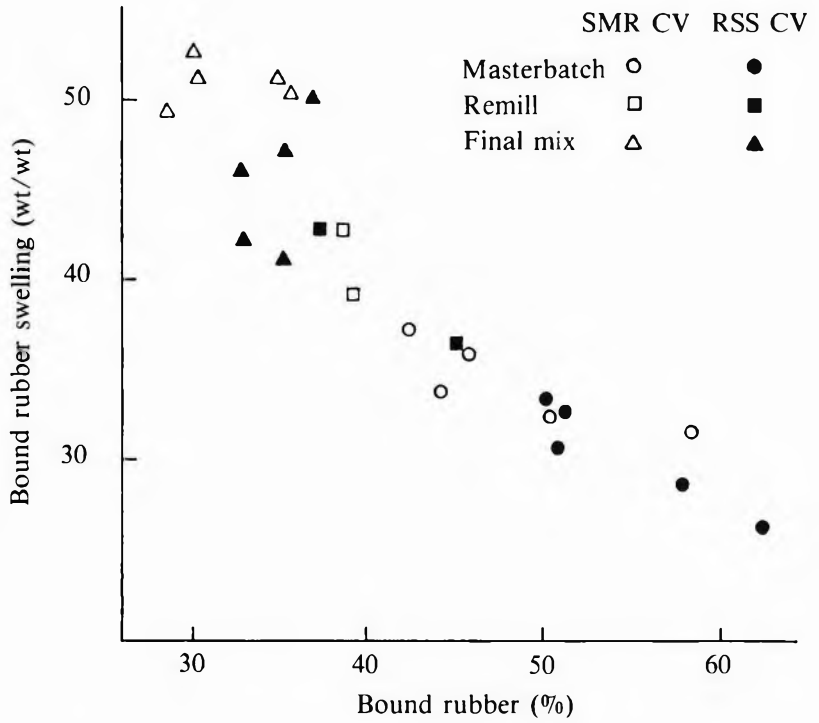

Figure 11. Correlation between bound rubber swelling and percent bound rubber for masterbatch, remill and final mixes.

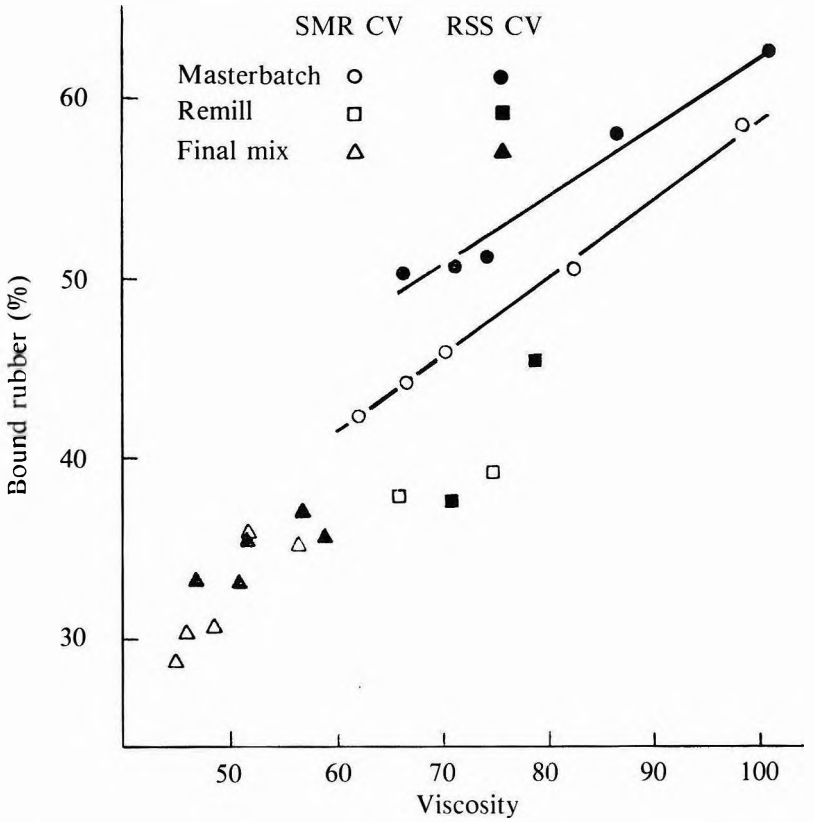

Figure 12. Dependence of percent bound rubber for masterbatch remill and final mixes on viscosity.

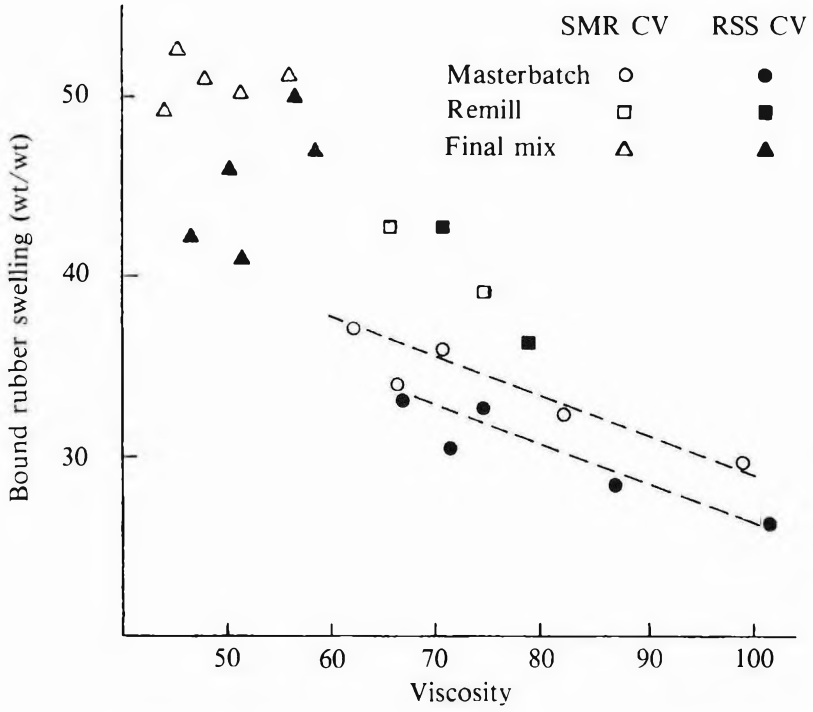

Figure 13. Dependence of bound rubber swelling for masterbatch, remill and final mixes on viscosity.

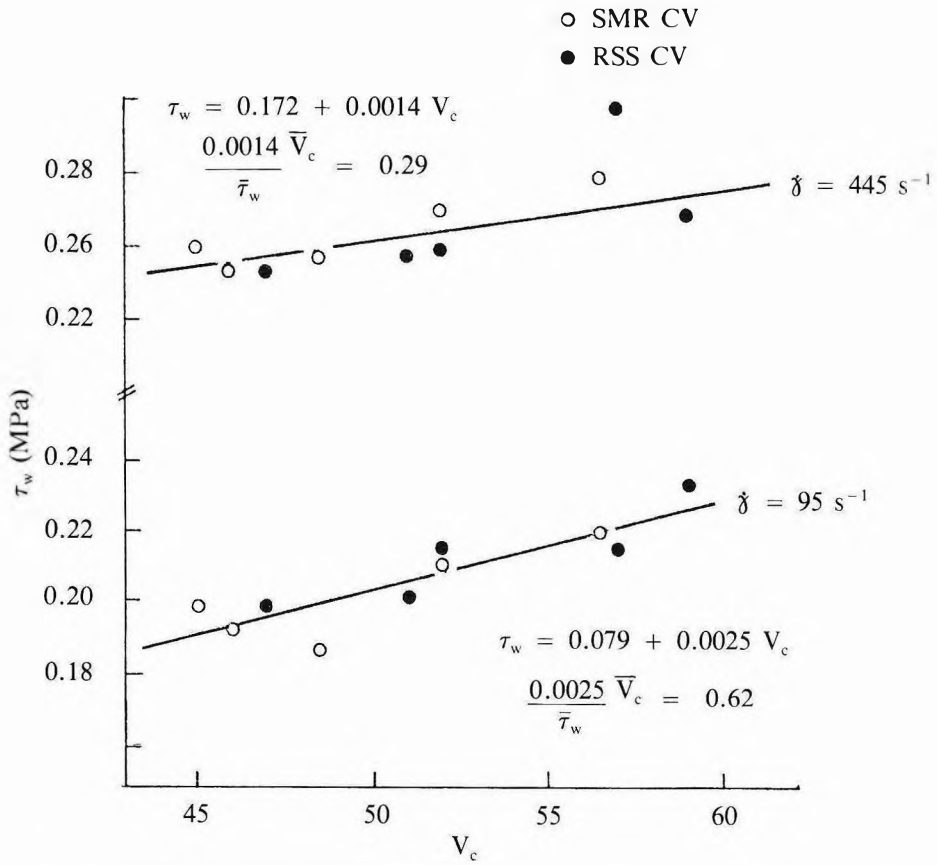

Figure 14. Correlation between wall shear stress and Mooney viscosity.

TABLE 7. CAPILLARY FLOW PARAMETERS FOR BANBURY-MIXED TREAD COMPOUND

Shear rate, τ (s^{-1})	Parameter	SMR CV					RSS CV				
		RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261	RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261
95	τ_1 (MPa)	0.240	0.244	0.271	0.236	0.256	0.250	0.264	0.282	0.250	0.267
	τ_2 (MPa)	0.718	0.647	0.736	0.621	0.674	0.709	0.709	0.727	0.691	0.736
	τ_w (MPa)	0.187	0.199	0.219	0.193	0.210	0.199	0.215	0.233	0.201	0.215
	e	22.7	18.0	18.8	17.7	17.7	20.5	18.4	17.0	19.5	19.4
445	τ_1 (MPa)	0.316	0.306	0.347	0.309	0.330	0.309	0.323	0.340	0.326	0.367
	τ_2 (MPa)	1.02	0.90	1.14	0.98	1.05	0.98	1.08	1.16	1.12	1.17
	τ_w (MPa)	0.238	0.240	0.259	0.234	0.250	0.234	0.239	0.249	0.238	0.278
	e	26.3	22.0	27.2	25.4	25.6	25.4	28.2	29.3	29.7	25.7
95	n	0.156	0.121	0.109	0.125	0.113	0.105	0.068	0.043	0.109	0.166
	S_1 (%)	42.2	39.5	40.5	42.4	41.6	39.6	43.9	39.8	43.5	41.9
	S_2 (%)	67.9	66.2	68.8	74.4	71.3	66.7	68.8	71.4	74.5	74.0
445	S_1 (%)	61.8	52.2	49.0	60.3	57.8	52.1	52.9	48.1	62.7	59.5
	S_2 (%)	134.5	99.2	102.6	133.1	124.0	101.9	111.1	104.2	143.1	140.1
	ML1+4, 100°C, V_C	48.5	45	56.5	46	52	47	52	59	51	57

τ_1 = Total shear stress L/D = 20
τ_2 = Total shear stress L/D = 2
τ_w = Wall shear stress
e = End correction
n = Flow index between $\gamma = 95\ s^{-1}$ and $\gamma = 445\ s^{-1}$
S_1 = Extrudate swell area percentage, L/D = 20
S_2 = Extrudate swell area percentage, L/D = 2

TABLE 8. FURTHER ANALYSIS OF THE DATA OF TABLE 7

Parameter	Shear rate γ s^{-1}	RSS CV		SMR CV		Δ (RSS CV — SMR CV)				
		Mean	S.D.	Mean	S.D.	RRIM 600	RRIM 623	RRIM 628	RRIM 700	PR 261
τ_w (MPa)	95	0.213	0.014	0.202	0.013	+ 0.012	+ 0.016	+ 0.014	+ 0.008	+ 0.005
τ_w (MPa)	445	0.248	0.018	0.244	0.010	− 0.004	− 0.001	− 0.010	+ 0.004	+ 0.028
e	95	19.0	1.3	19.0	2.1	− 2.2	+ 0.4	− 1.8	+ 1.8	+ 1.7
e	445	27.7	2.0	25.3	2.0	− 0.9	+ 6.2	+ 2.1	+ 4.3	+ 0.1
S_1	95	41.7	2.0	41.2	1.2	−2.6	+ 4.4	− 0.7	+ 1.1	+ 0.3
S_2	95	71.1	3.3	69.7	3.2	− 1.2	+ 2.6	+ 2.6	+ 0.1	+ 2.7
S_2-S_1	95	29.3	3.2	28.5	2.5	+ 1.4	− 1.8	+ 3.3	− 1.0	+ 2.4
S_1	445	55.1	5.9	56.3	5.4	− 9.7	+ 0.4	− 0.9	+ 2.4	+ 1.7
S_2	445	120.1	20.0	118.7	16.8	−32.6	+11.9	+ 1.6	+10.0	+16.1
S_2-S_1	445	65.0	14.5	62.4	11.8	−22.9	+11.5	+ 2.5	+ 7.6	+14.4

show greater discrimination. Once again, sheet and crumb-based materials conform to the same regressions. Values of the flow index, *n*, for a power law flow curve, have been calculated from the two data points only, and, while the precision of these values must therefore be limited, *n* is larger for SMR CV than for RSS CV for four of the five clones (the data for RSS CV — PR 261 appear anomolous in several respects). For RSS CV — RRIM 623 and RRIM 628, *n* is exceptionally low. Values of *e*, again estimated from only two data points at each of the two shear rates, are far more self-consistent. Sheet and crumb materials do not differ significantly in *e*, and hence in the equivalent 'end pressure' $P_0 = e\pi_w$.

Extrudate swell follows the expected pattern, in that swell is greater at higher shear rate and the dependence on shear rate is greater for the die of low *L/D* ratio (*Figures 15* and *16*). However, over the very limited range of shear stress covered by the ten samples, there are no obvious trends of swell with stress even though the precision of the data would be expected to be greater than the observed scatter. In these circumstances it is perhaps not surprising that systematic differences in swell between sheet and crumb-based materials are not apparent. However, the grade mean values of S_1, S_2 and S_1-S_2 at each of the two shear rates indicate that differences in swell due to raw rubber production procedure cannot be large.

CONCLUSIONS

The parity in properties and performance between viscosity stabilised sheet and crumb materials established for raw rubber is in large measure also found in the mixing and processing behaviour of a typical tread stock. Only in the case of the initial formation of bound rubber or carbon gel, a parameter indicative of rubber black interaction, is there evidence for an obvious effect of raw rubber production procedure, but even here this difference is eliminated in the inevitable further working during final mixing.

July 1988

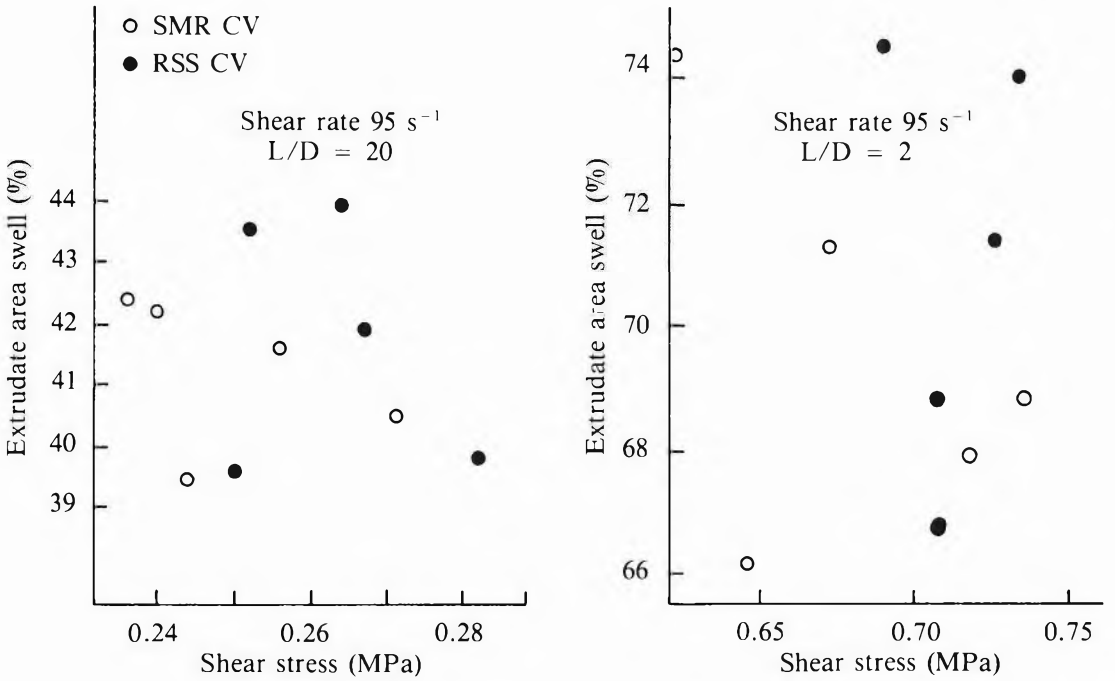

Figure 15. Dependence of extrudate swell at 95 s^{-1} on shear stress.

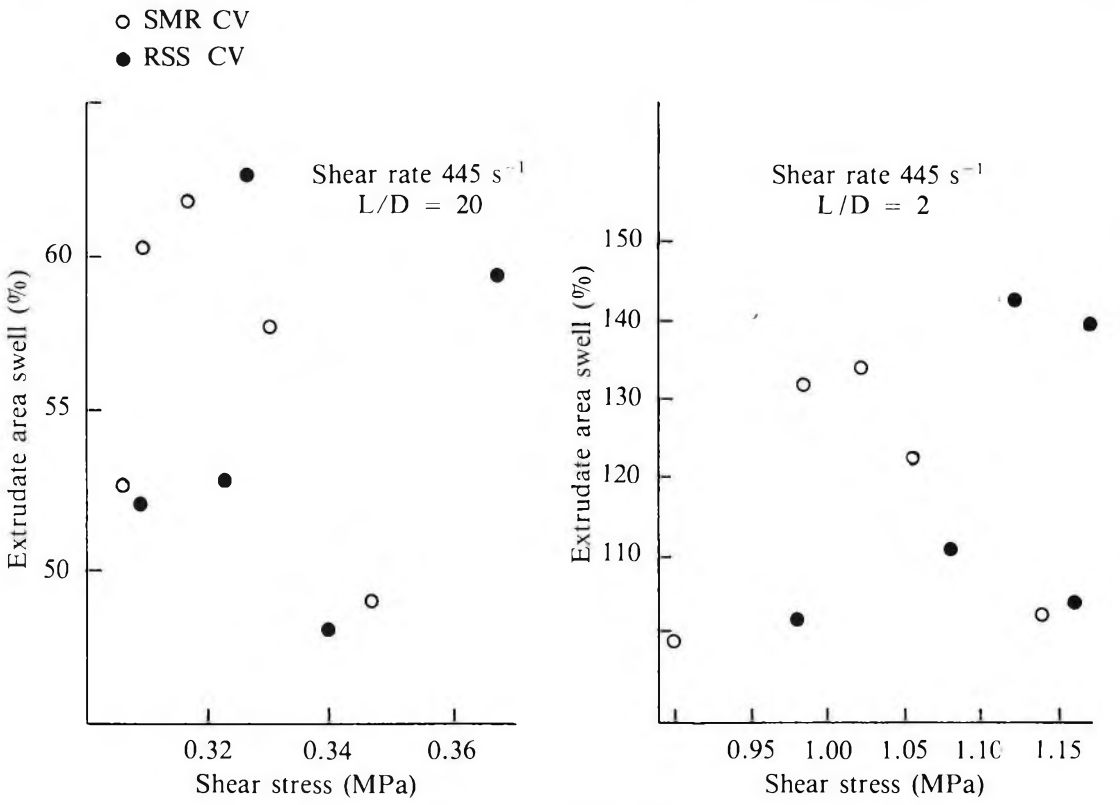

Figure 16. Dependence of extrudate swell at 445 s^{-1} on shear stress.

REFERENCES

1. BRISTOW, G.M. AND SEARS, A.G. (1988) A New Comparison of Sheet and Crumb Rubber. Part I. Raw Rubber Composition and Rheology. *J. nat. Rubb. Res.*, **3(4)**, 223.

2. BRISTOW, G.M. AND SEARS, A.G. (1984) Correlation between Raw Rubber Breakdown and Mixing Performance in an ISAF Tread Stock. *NR Technol.*, **15(1)**, 1.

3. LIM, H.S. AND LIM, C.L. (1985) A Test for Assessing the Breakdown and Mixing Behaviour of Viscosity-stabilized Grades of Natural Rubber. *Proc. Int. Rubb. Conf. 1985 Kuala Lumpur*, **2**, 225.

4. RUBBER RESEARCH INSTITUTE OF MALAYSIA (1970) Test Methods for Standard Malaysian Rubbers. *SMR Bull. No. 7.*

5. VAN BUSKIRK, P.R., TURETZKY, S.B. AND GUNBERG, P.F. (1975) Practical Parameters for Mixing. *Rubb. Chem. Technol.*, **48**, 577.

6. SEARS, A.G. (1987) Unpublished data. Malaysian Rubber Producers' Research Association.

7. MEDALIA, A.I. AND WALKER, D.P. Evaluating Dispersion of Carbon Black in Rubber. *Technical Report RC-124, Revision No. 2.* USA: Cabot Corporation.

8. LIM, C.L. AND ONG, E.L. (1985) Breakdown Behaviour of Natural Rubber and Its Influence on Processability. *Proc. Int. Rubb. Conf. 1985 Kuala Lumpur*, **2**, 557.

9. SEARS, A.G. (1987) Unpublished data. Malaysian Rubber Producers' Research Association.

J. nat. Rubb. Res., **4(1)**, 41-46

Ultrastructure of Rubber Particles in PA 80 Latex. II. Effects of Storage

SAMSIDAR HAMZAH*, J.B. GOMEZ* AND P.S. RAMA RAO*

As a result of the sensitivity of PA 80 latex to 5% $KMnO_4$ fixation in differentiating vulcanised and unvulcanised particles or zones of these particles, this method was again used to find the effects of storage. Latices examined were from various stages of vulcanisation which have been stored for one and six months.

Vulcanisation as judged from the increase in intensity of staining of the particle interior was found to be progressive during storage even when the stage of vulcanisation was preliminary i.e. *when the dispersion mixture was just added. The shell thickness of the rubber particles too is increased. Evidence from elsewhere has shown that there is an increase in free and total sulphur and gel content on storage. The electron microscopic results are consistent with these findings.*

Even though all the specification limits have been met at the producers' level, there are still some complaints from local as well as overseas users of PA 80. Most of the complaints relate to the calendered product of PA 80 having poor surface finish and often displaying discrete lumps of uneven dispersion[1].

Storage may have contributed to the problems encountered especially during the long course of transportation or shipment. It is with this problem in mind that this study was undertaken. The effect of storage of PA 80 latex is also studied for fundamental reasons, despite the fact that PA 80 may not be exported in that form any more. The changes detected, as in an earlier study[2] have managed to differentiate and in some ways, explain what happens during storage. Observations are made on one and six months' storage under controlled conditions.

MATERIALS AND METHODS

The same latex samples that were used in the last study[2], collected at the various stages of vulcanisation, were kept at room temperature. These were sampled one and six months later for electron microscopy. Samples were subjected to similar procedures for electron microscopic examination as described earlier[2].

OBSERVATIONS AND DISCUSSION

Osmium Fixation

In general, osmium fixation did not seem to show distinctive differences in the microstructure of the rubber particles when these different samples were stored. It is however worthy to note that there are changes in the ammoniated sample especially that which has been stored for six months. As has been shown previously[2], the addition of 0.7% NH_3 to latex affected the elasticity of the membrane of the rubber particles *i.e.* there was a change from a rigid boundary to a crenulated one.

On storage, the boundaries of the rubber particles still remained crenulated perhaps less; but not all the particles were showing uniform electron density *(Figure 1B)*. These odd particles have electron density grading from darker in the periphery to lighter in the interior. There are even some particles which contain fibrillar material within the empty-looking interior. These are reminiscent of the lipid particles in their different stages of formation in the Frey-Wyssling (F.W.) complexes[3]. The crescent-like particle in *Figure 1B* is most probably a component from a broken F.W. complex.

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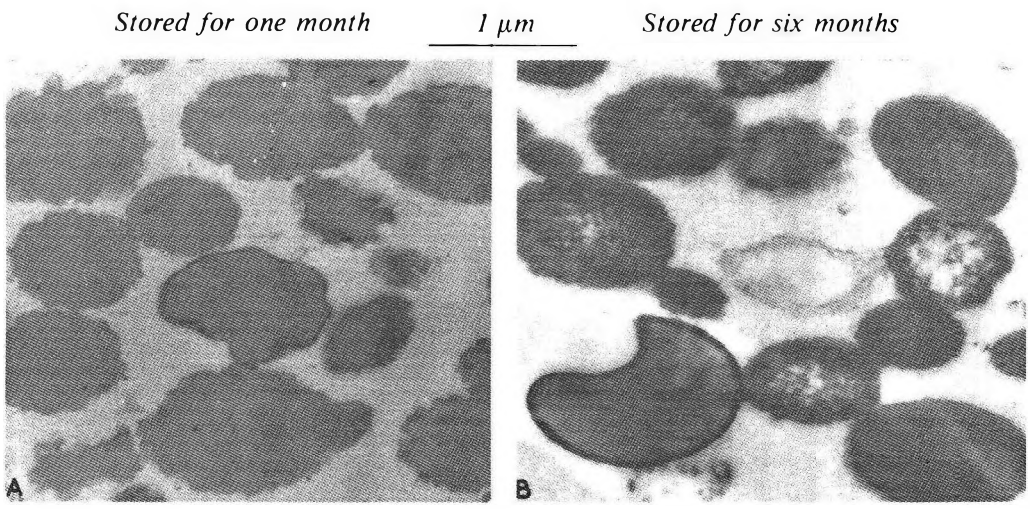

Figure 1. Sections of 0.7% ammoniated rubber particles stored for one month and six months; fixed in OsO_4 and stained in lead citrate.

Permanganate Fixation

$KMnO_4$ fixation was found to be the more sensitive fixative in detecting micro-structural changes in rubber particles during sulphur vulcanisation[2]. Only the stained sections are discussed here as they are enhanced further by the addition reaction of osmium tetroxide.

The stored ammoniated rubber particles are shown in *Figures 2A* and *2B*. Gross changes were not apparent in these rubber particles but there is an indication of a slight increase in the shell thickness at six months' storage (an increase of approximately 1000 Å from the one-month storage in the limited number of particles measured). It is possible that this increase in shell thickness is somewhat related to the change in composition of membrane or related structures of stored ammoniated latex as some studies have indicated[4]. Stored ammoniated latex has also been shown to have an increase in the MST[5].

What is interesting at the 0-h stage (*i.e.* immediately after adding the vulcanising dispersion) is the speckled interior of these particles ranging from a few dots in the one-month stored sample *(Figure 2C)* to a visible speckled-ball in the six-month stored sample *(Figure 2D)*. This speckled interior in the unstored sample was only seen 2 h after putting the steam on *i.e.* at 77°C. With this observation, it can be inferred that vulcanisation is still taking place during storage, based on the resistance of the particles to oxidation by permanganate during the fixation procedure.

Another feature at the 0-h stage, not generally observed in the unstored sample, is the rupturing of the particle shells (representing the gel layer), especially in the bigger particles and in the six-month stored sample (*Figures 2C* and *2D*). This may have been attributed partly to the brittleness of the shell and also to the swelling of the sol in the embedding medium as a result of being only partially vulcanised. Fresh, unvulcanised rubber particles fixed in $KMnO_4$ also sometimes experience shell rupture, but this is not excessive and is mainly considered to be due to the fixation releasing some gaseous by-products of the oxidation reaction.

As the process of vulcanisation progresses, the intensity of the interior of the shell increases proportionately; but more intensely in the six-month stored 80:20 mixture *(Figure 2P)*. This means that these latter particles are more vulcanised than the one-month sample. Other features which are also indicative of being more vulcanised are the almost intact shell, perhaps

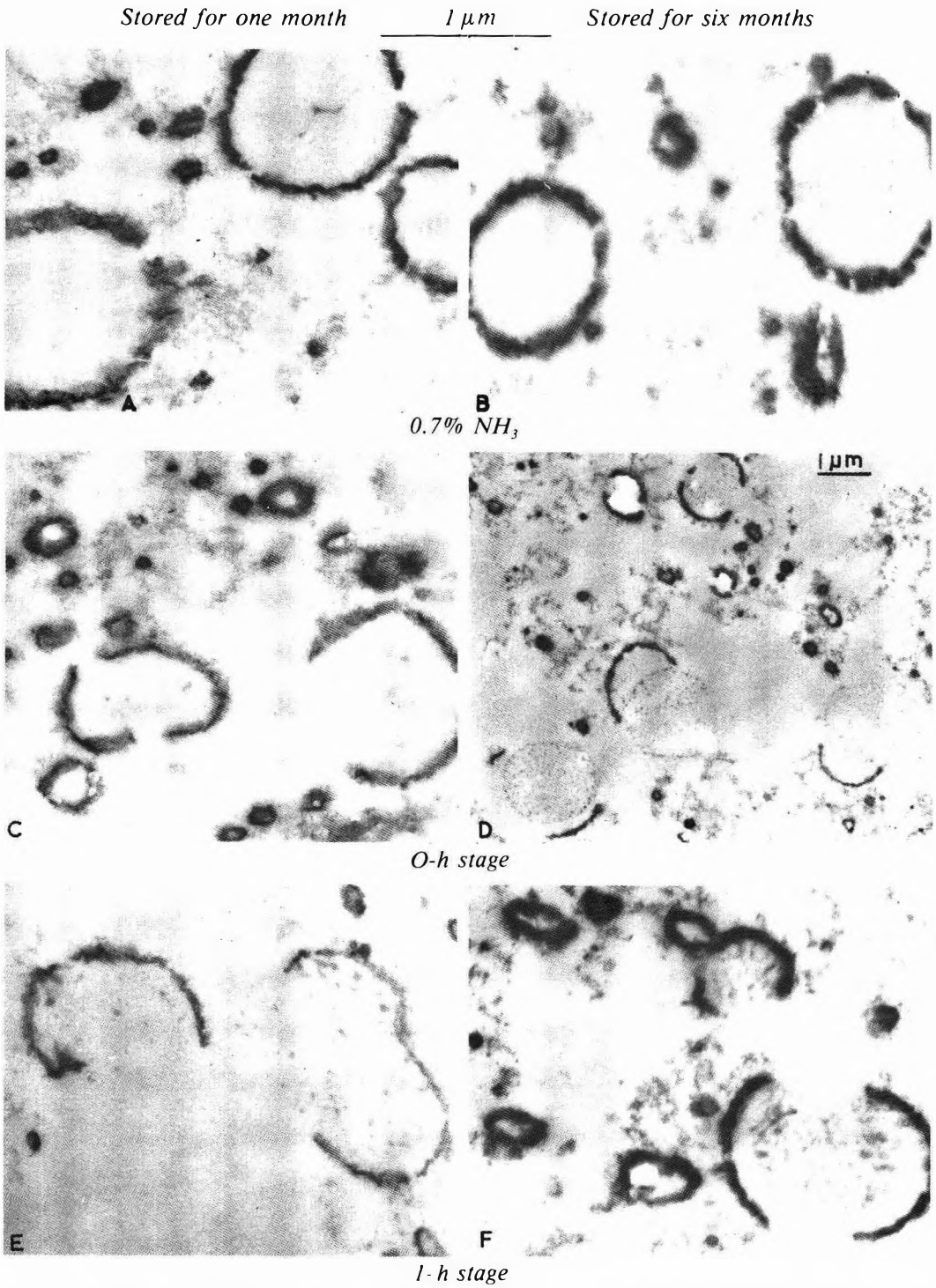

Figure 2. Sections of stored (one and six months) rubber particles from various stages of vulcanisation; fixed in $KMnO_4$ and post-stained with osmium vapour.

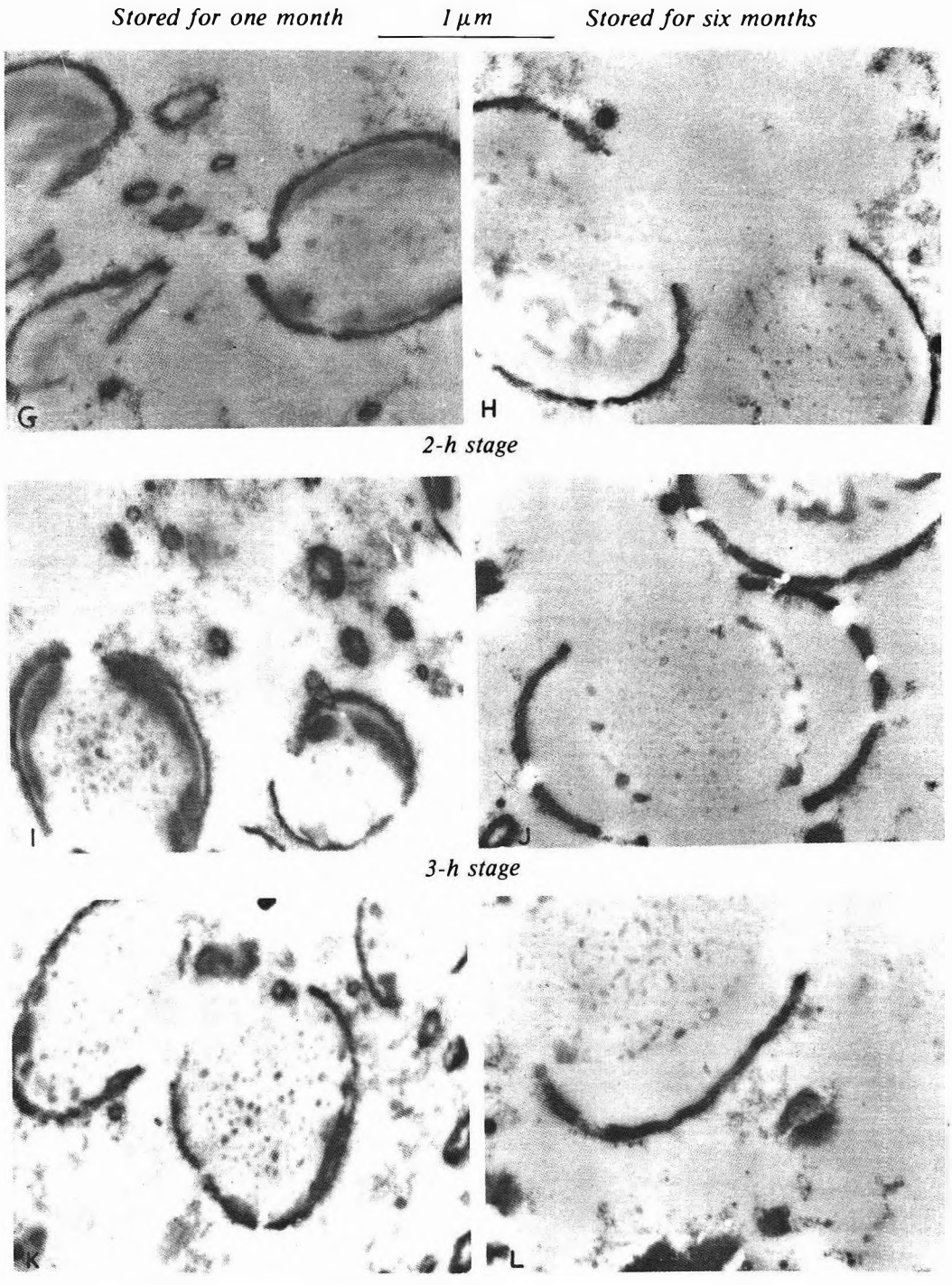

Figure 2. Sections of stored (one and six months) rubber particles from various stages of vulcanisation; fixed in $KMnO_4$ and post-stained with osmium vapour (contd).

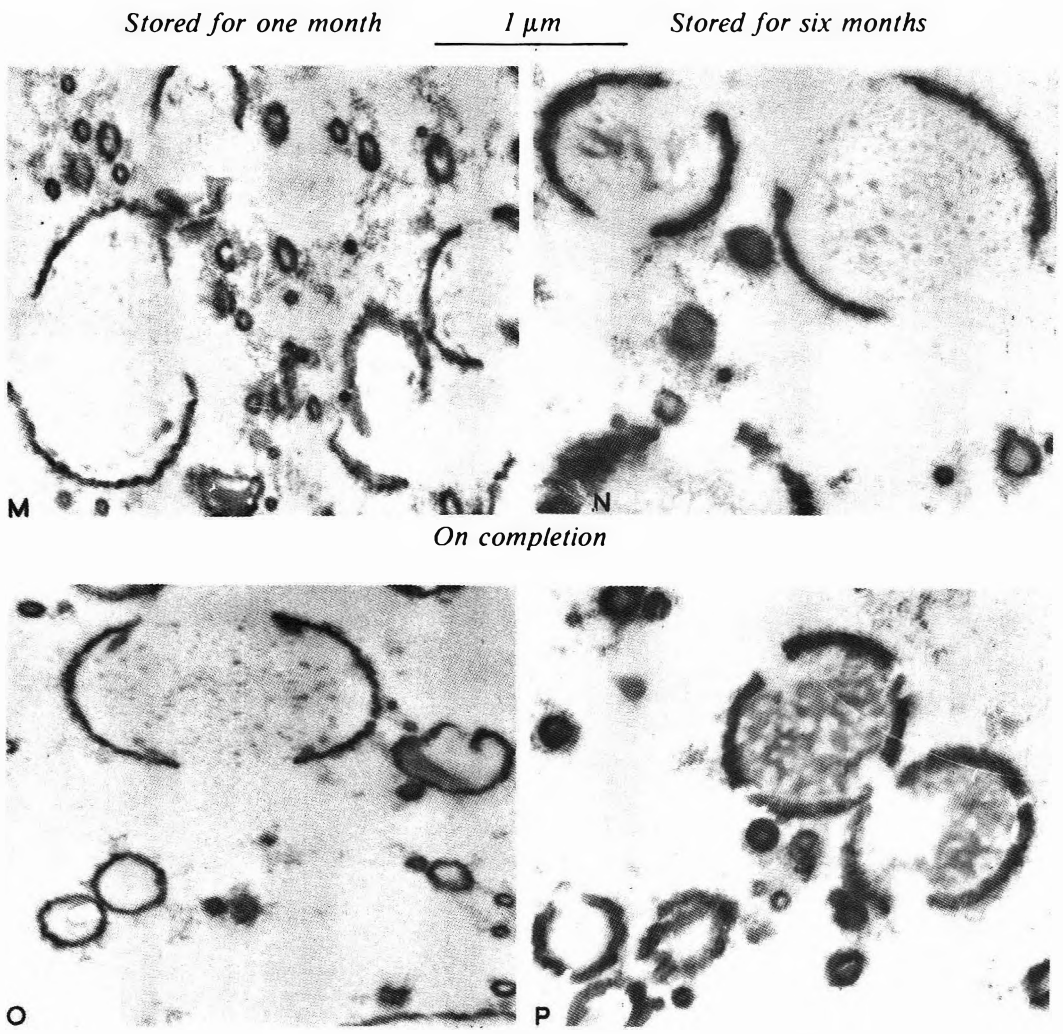

Figure 2. Sections of stored (one and six months) rubber particles from various stages of vulcanisation; fixed in $KMnO_4$ and post-stained with osmium vapour (contd).

with a small rupture, and close adherence of sol to gel (shell) indicating no swelling or limited swelling.

In the other stages of vulcanisation, rupturing of the shell is also extensive especially in the six-month stored samples. The limited shell rupture in the one-month stored sample (from the 2-h stage to the 5-h stage) is probably due to the presence of an electron-dense band very close to the shell (*Figures 2G, 2I* and *2K*). This may represent the external part of the sol which is highly vulcanised, compared to the interior, which did not succumb to swelling. Such bands are, however, not clearly seen in the six-month stored samples.

Storage has also an effect on the shell thickness of the rubber particles sampled during the various stages of vulcanisation. The thick-

ness of the shell after six months' storage (average of 650 Å) shows an increase over the unstored samples (average of 400 Å) and one-month stored samples (average of 200 Å). What is implied by the increase in thickness of the shell may well have been related to the increase in gel content as shown by *Table 1*. Even though these values were not obtained from the experimental samples (from a commercial factory) yet the values do show an increase on storage. The increase in free sulphur and total sulphur on storage as shown in this table could also be related to the increase in intensity of the internal sol observed as the samples were stored.

TABLE 1. EFFECTS OF STORAGE ON THE PHYSICAL PROPERTIES OF PA 80 LATEX[a]

Property	Storage		
	0 month	3 months	6 months
Mooney viscosity, V_R	71.7	71.7	78.7
Swell (%)	8.8	9.7	9.1
Gel content	82.7	84.9	85.5
Free sulphur (%)	0.3	0.4	NA
Total sulphur	1.6	1.7	NA

NA = Not available

[a]Values derived from means of three samples made from one lot (batch).

CONCLUSION

The increase in the intensity of staining of the electron-dense specks within the shells of the $KMnO_4$ fixed stored samples could be envisaged as an increase in the degree of vulcanisation and consequent increase of crosslink density. It is interesting to note that with greater duration of storage, the inner part of the rubber particle not only has a higher electron density but is more resistant to permanganate oxidation under the conditions it is exposed to. This is consistent with the hypothesis that storage increases the degree of vulcanisation of each particle presumably due to the residual effects of the vulcanising dispersion present in the mixture. Probably, savings on chemicals could be effected by a finer degree of control on the dispersion mixture.

The study also demonstrates that the permanganate fixation technique is a sensitive technique for electron microscopic examination of rubber particles subjected to modification by vulcanisation and similar phenomena.

This study is limited to stored latex in the vulcanised form and does not throw light on the effects of vulcanisation and subsequent processing of rubber on the conditions of storage. For example, it does not throw light on the crepe or block rubbers made from PA 80. It is suggested that such a study may have inherent values associated with it.

ACKNOWLEDGEMENT

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October 1988

REFERENCES

1. MUNIANDY, V. (1987) Private communication. Rubber Research Institute of Malaysia.
2. SAMSIDAR HAMZAH, GOMEZ, J.B. AND RAMA RAO, P.S. (1987) Ultrastructure of Rubber Particles in PA 80 Latex. I. Changes during Sulphur Vulcanisation Reaction. *J. nat. Rubb. Res.*, **2(2)**, 118.
3. GOMEZ, J.B. AND SAMSIDAR HAMZAH (1988) The Frey-Wyssling Complex in *Hevea* Latex — the Uniqueness of the Organelle. Paper submitted to *J. nat. Rubb. Res.*
4. HASMA, H. (1988) The Role of Lipids Associated with the Rubber Particles on the Mechanical Stability of Latex Concentrate. Private communication. Rubber Research Institute of Malaysia.
5. CHIN, H.C., SINGH, M.M. AND LOKE, S.E. (1978) Effect of Storage on the Properties of High-ammonia-preserved *Hevea* Latex Concentrate. *Proc. Int. Polym. Latex Conf.* London: Plastics and Rubber Institute.

J. nat. Rubb. Res., **4(1)**, 47-55

Characterisation of Rubber Particle Destabilisation by B-serum and Bark Sap of Hevea brasiliensis

H.Y. YEANG*

Destabilisation of rubber particle suspensions as indicated by their flocculation, creaming and coagulation can be induced by the addition of small quantities (8%) of either B-serum or bark sap of Hevea brasiliensis. *The responses elicited depended on the presence of C-serum, the concentration of rubber particles and the source of the rubber particles (whether they were low or high density particles) in the suspensions. Under appropriate conditions, instantaneous flocculation of rubber particles can be induced by B-serum or bark sap. The rapidity of this response was consistent with its possible involvement in latex vessel plugging. The destabilisation of rubber particles by B-serum was markedly inhibited when C-serum was present in the suspension whereas destabilisation was largely unaffected when induced by bark sap. In fact, coagulation could be induced by bark sap only in the presence of C-serum. The denser rubber particles from* Zone 2 *of centrifuged latex were more sensitive to destabilisation than those from* Zone 1 *which constituted the major proportion of the rubber in latex.*

Plugs that are formed progressively at the cut ends of severed latex vessels when the rubber tree is tapped inhibit latex exudation[1,2,3]. The plugging behaviour of the tree thus influences the duration of latex flow and yield output. Latex vessel plugs are composed mainly of destabilised and coagulated rubber particles together with destabilised lutoids[4]. Hence, the destabilisation of latex as it exudes from the tree plays an important role in the formation of latex vessel plugs. Latex destabilisation also features prominently in the latex vessels of trees suffering from dryness[5] which is a disorder of the rubber tree where the tapping cut ceases to yield partially or completely.

Two native latex destabilising agents are known in *Hevea:* B-serum, which is the fluid content of lutoids found in the latex and bark sap which is the fluid content of bark tissue. Although various characteristics of the destabilisation of latex or rubber particle suspensions by B-serum[6,7,8] and bark sap[9-12] have been described, it is often difficult to make comparative assessments of such collated information because of the dissimilar experimental approaches employed by different workers. For example, since B-serum activity is inhibited by C-serum[6], B-serum reactions would differ depending on whether they are carried out in the presence or absence of C-serum. The destabilisation response is also affected by the type of rubber particles used in the reaction. While much of the previous work has been based on rubber particles obtained from the major rubber cream fraction (Moir's[13] *Zone 1*) of centrifuged latex, it has recently been shown[12] that the denser rubber particles from *Zones 2* and *3* are far more susceptible to destabilisation by bark sap. To complicate matters further, quantification of latex destabilisation has been based on different criteria, principally the onset of flocculation, creaming, or coagulation of the rubber particles in latex or a rubber particle suspension. There has been some confusion and uncertainty as to whether these three parameters do in fact measure one and the same variable. It has been observed, for example, that rubber particle suspensions often flocculate without subsequent formation of a coagulum[7].

The present study was undertaken to characterise the destabilisation of rubber particle

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suspensions by B-serum and by bark sap as influenced by the:

- Source of the rubber particles: whether they were low density rubber particles from the rubber cream fraction of centrifuged latex (Moir's *Zone 1*) or high density rubber particles from *Zones 2* and *3*
- Rubber particle content in the suspension
- Presence of C-serum in the suspending medium.

In each instance, destabilisation was assessed in terms of the:

- Flocculation of rubber particles
- Creaming of rubber particles
- Coagulation of rubber particles.

MATERIALS AND METHODS

The flow of latex for the first half-hour was collected into chilled containers from RRIM 600 trees tapped ½S d/2 on *Panel BO*–2. The latex was centrifuged in a Sorvall RC-2B centrifuge at 19 000 r.p.m. (44 000 g max.) at 3°C–4°C to obtain the basic centrifugation zones described by Moir[13] *(Figure 1)*. Rubber cream from *Zone 1* was sampled after centrifugation of the latex for 1 h while *Zone 2* was recovered after centrifugation for 2 h. The additional hour of centrifugation had the effect of transferring some of the high density rubber particles from *Zone 3* to *Zone 2*[13]. Thus, *Zone 2* in this instance also contained rubber particles that would otherwise have been deposited in *Zone 3* had the duration of centrifugation been the usual 1 h. The rubber particle and C-serum contents in the *Zone 1* and *Zone 2* samples were initially estimated from the proportion of dry solids in the samples. Using these guide figures, suspensions of 1% and 5% rubber particle content in varying concentrations of C-serum were prepared by resuspending the samples in appropriate mixtures of C-serum and water. The suspensions were filtered through muslin cloth before use.

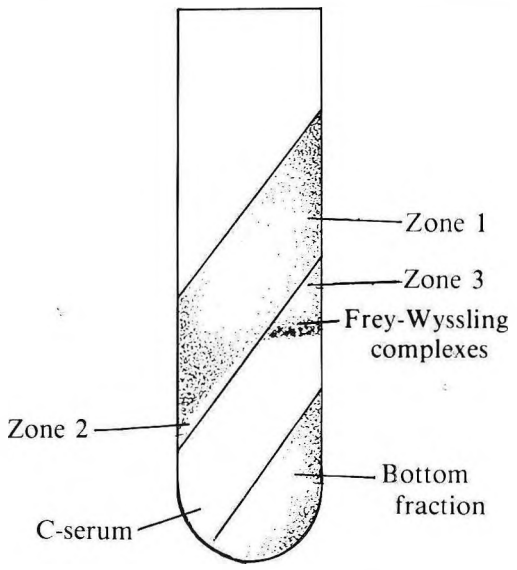

Figure 1. Fractionation of fresh latex by high-speed centrifugation.

B-serum was prepared as described previously[12] by repeated freezing and thawing of the bottom fraction of centrifuged latex to rupture the lutoids. To prepare bark sap, bark shavings excised from the tapping cut were pressed between pinch rollers as described previously[12]. The extract was cleared by low-speed centrifugation.

Immediately on adding the destabiliser (8% B-serum or 8% bark sap) to the rubber particle suspension in the test tube, the contents were mixed for 2–3 s using a vortex mixer. Destabilisation of the rubber particle suspensions was characterised in terms of flocculation, creaming or coagulation of the particles. Flocculation was quantified by visual score of the amount of floccules left behind on the test tube wall after vortex mixing *(Figure 2)*. The rubber particle suspensions were checked for the formation of a layer of cream 15 min after the destabiliser was added. The test tubes were checked for coagulation 50 min after addition of the destabiliser. Coagulation was deemed to have occurred when the agglomeration and gellation of rubber particles had proceeded to the extent that a cohesive mass could be picked up using a pair of forceps.

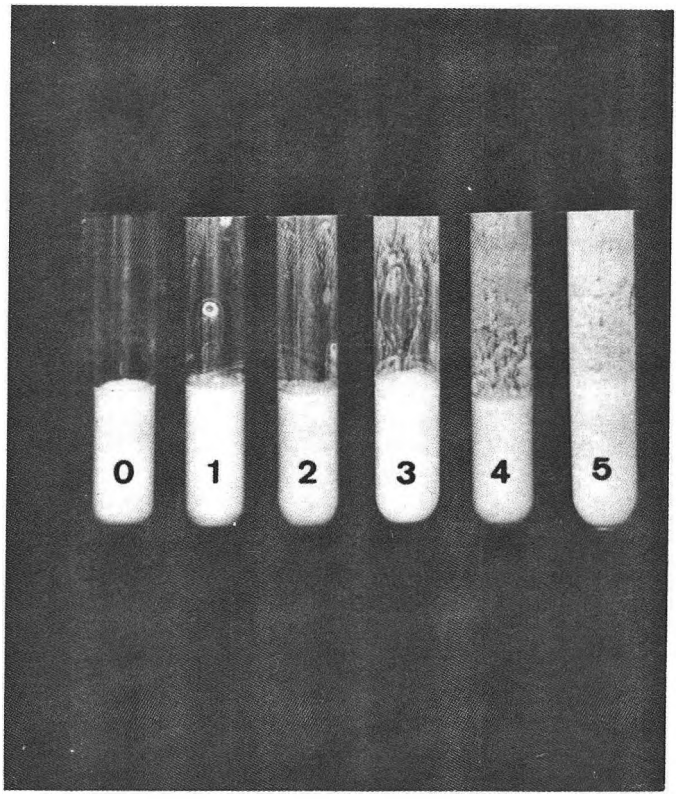

Figure 2. Visual scoring of rubber particle flocculation based on the amount of rubber floccules adhering to the sides of the test tube after vortex-mixing.

The concentration of C-serum in the test suspension refers to the proportion of C-serum in the suspending medium after addition of the destabiliser. Concentrations of rubber particles, B-serum and bark sap refer to the final concentrations in 2 ml reaction mixtures.

RESULTS

All three responses to destabilisation of rubber particle suspensions, *viz.* flocculation, creaming and coagulation of the rubber particles, could be induced by the addition of 8% of either B-serum or bark sap. These responses were elicited to varying extents under different experimental conditions, depending on the presence of C-serum in the suspension, the concentration of rubber particles in the suspension and the source of the rubber particles (whether they were low-density particles from Moir's *Zone 1* of centrifuged latex or higher density particles from *Zone 2*). Details of the flocculation, creaming and coagulation responses are presented in *Table 1* for 1% rubber particle suspensions and in *Table 2* for 5% rubber particle suspensions. The salient features are as follows.

Flocculation

Flocculation occurred in suspensions of rubber particles prepared from either *Zone 1* or *Zone 2* of centrifuged latex. *Zone 2* particles appeared to flocculate better in most instances despite the fact that they were presumably less visible since in centrifuged latex, *Zone 2* was more translucent compared with the opaque white *Zone 1*.

A suspension of 5% rubber particles flocculated better than a 1% suspension.

TABLE 1. EFFECT OF 8% B-SERUM OR 8% BARK SAP ON THE DESTABILISATION OF 1% RUBBER PARTICLE SUSPENSIONS IN VARYING C-SERUM CONCENTRATIONS

Response[a]	Destabiliser	Zone 1 rubber particles C-serum in suspending medium						Zone 2 rubber particles C-serum in suspending medium					
		1%	5%	10%	20%	50%	92%	1%	5%	10%	20%	50%	92%
Flocculation	B-serum	1.3	1.3	0.9	0.8	0	0	2.0	2.0	2.0	2.0	0.3	0
	Bark sap	0.9	0.9	1.1	0.9	0.4	0.6	1.8	1.8	1.0	1.0	1.0	1.0
Creaming	B-serum	1.8	1.4	1.0	0.5	0	0	1.8	0.9	0.5	0.3	0	0
	Bark sap	1.3	0.3	0	0	0	0	0.3	0	0	0	0	0
Coagulation	B-serum	0	0	0	0	0	0	0	0	0	0	0	0
	Bark sap	0	0	0	0	0	0	0	0	0	0	0	0

[a] Flocculation scored on a scale of 0 to 5: 0 = no flocculation; 5 = very strong flocculation
Creaming scored on a scale of 0 to 2: 0 = no creaming; 1 = poorly defined cream layer; 2 = well defined cream layer
Coagulation scores: 0 = no coagulation
Results are the means of four experiments

TABLE 2. EFFECT OF 8% B-SERUM OR 8% BARK SAP ON THE DESTABILISATION OF 5% RUBBER PARTICLE SUSPENSIONS IN VARYING C-SERUM CONCENTRATIONS

Response[a]	Destabiliser	Zone 1 rubber particles C-serum in suspending medium					Zone 2 rubber particles C-serum in suspending medium				
		3%	10%	20%	50%	92%	3%	10%	20%	50%	92%
Flocculation	B-serum	3.5	3.0	3.0	2.3	1.6	3.3	3.0	2.8	1.0	0
	Bark sap	4.0	3.5	3.8	3.3	3.0	4.5	4.5	4.3	4.0	4.0
Creaming	B-serum	0	0	0	0	0	0	0	0	0	0
	Bark sap	0	0	0	0	0	0	0	0	0	0
Coagulation	B-serum	0	0	0	0	0	a	b	0	0	0
	Bark sap	0	0	0	0	0	0	0	0	c	d

[a] Flocculation scored on a scale of 0 to 5: 0 = no flocculation; 5 = very strong flocculation
Creaming scores: 0 = no creaming
Coagulation scores: 0 = no coagulation; a = coagulation in twenty-three out of twenty-four experiments; b = coagulation in one out of four experiments; c = partial coagulation in two out of four experiments; d = coagulation in nineteen out of twenty-five experiments.
Results are the means of four experiments.

Flocculation, when induced by *bark sap,* was not markedly influenced by the concentration of C-serum present in the suspension although the reaction tended to be stronger at lower C-serum concentrations.

On the other hand, flocculation evoked by *B-serum* was strongly inhibited by the presence of C-serum. This was especially marked with *Zone 2* rubber particles where flocculation in both 1% or 5% rubber particle suspensions was completely suppressed when C-serum concentration in the suspending medium was 92% *(Figure 3).* With *Zone 1* rubber particles, complete inhibition of flocculation at high C-serum concentration by B-serum only

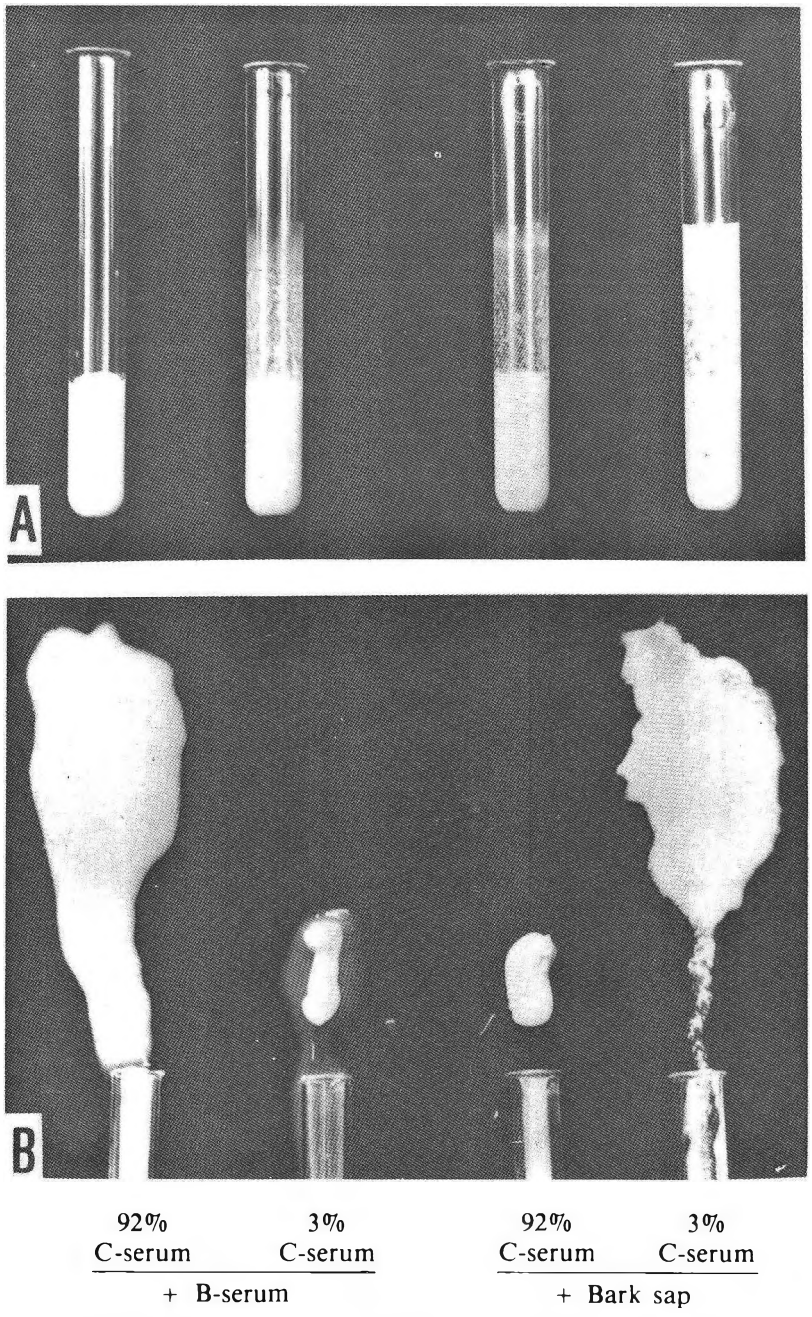

Figure 3. Flocculation and coagulation of 5% rubber particle suspensions induced by 8% B-serum or 8% bark sap. The rubber particles were from Zone 2 *of centrifuged latex and were suspended in media containing 92% or 3% C-serum.* A: *Latex flocs left on the walls of the test tubes after vortex mixing of the contents when the destabilisers were added;* B: *Contents of the same tubes after 50 min*

occurred when the rubber particle content was low (1%). When the rubber particle content was raised to 5%, some flocculation occurred even when the suspending medium consisted of 92% C-serum.

Creaming

Creaming occurred in suspensions of rubber particles prepared from either *Zone 1* or *Zone 2* of centrifuged latex. *Zone 1* particles creamed more readily, this being attributable to some extent at least by its lower density. B-serum was more effective than bark sap in evoking the creaming response *(Figure 4).*

Creaming occurred only when the rubber content in the suspension was low (1%). The response was poor when the concentration of rubber particles was raised to 5%.

Creaming occurred only when the C-serum concentration in the suspending medium was low *(Figure 4), i.e.* about 3% for bark sap and below 20% for B-serum.

Coagulation

Coagulation occurred in suspensions of rubber particles prepared from *Zone 2* but not from *Zone 1* of centrifuged latex. It occurred only when the rubber particle content was sufficiently high (5%). Suspensions of 1% rubber particles did not coagulate.

The effect of C-serum on the coagulation response depended on whether it was B-serum or bark sap that was being used as the destabiliser. When *B-serum* was added, coagulation only occurred in the substantial *absence* of C-serum *(Figure 3).* Coagulation was strongly

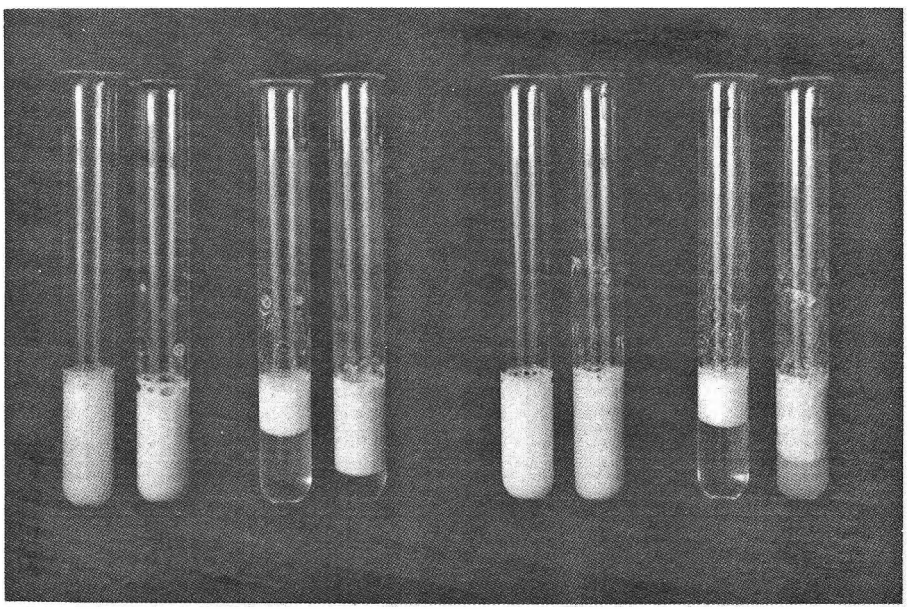

Figure 4. Creaming in 1% rubber particle suspensions induced by 8% B-serum or 8% bark sap. Rubber particles from Zone 1 *or* Zone 2 *of centrifuged latex were suspended in media containing 92% or 1% C-serum. For each pair of test tubes, B-serum had been added to the left test tube and bark sap to the right test tube. (Photographed after 30 min)*

inhibited by 10% C-serum in the suspending medium, the inhibition being complete at about 20% C-serum.

With *bark sap* as the destabiliser, the *presence* of C-serum was obligatory for coagulation to take place. Coagulation was observed when C-serum concentration in the suspending medium was 92% while no coagulation occurred at below 50% C-serum despite extensive flocculation in the suspension *(Figure 3)*.

The various reactions described above, *viz.* the flocculation, creaming and coagulation of rubber particle suspensions, showed good repeatability generally, with the exception of the coagulation response induced by bark sap. There were a few instances (six out of twenty-five observations) where bark sap inexplicably failed to invoke the coagulation response despite the presence of all conducive experimental conditions. Copious flocculation was usually observed on these occasions.

The principal responses to B-serum and bark sap in the destabilisation of rubber particles under different experimental conditions are summarised in *Figure 5*.

DISCUSSION

Various parameters governing rubber particle destabilisation were examined to determine the extent they were identifiable with the destabilisation of latex in the rubber tree in connection with latex vessel plugging and tree dryness.

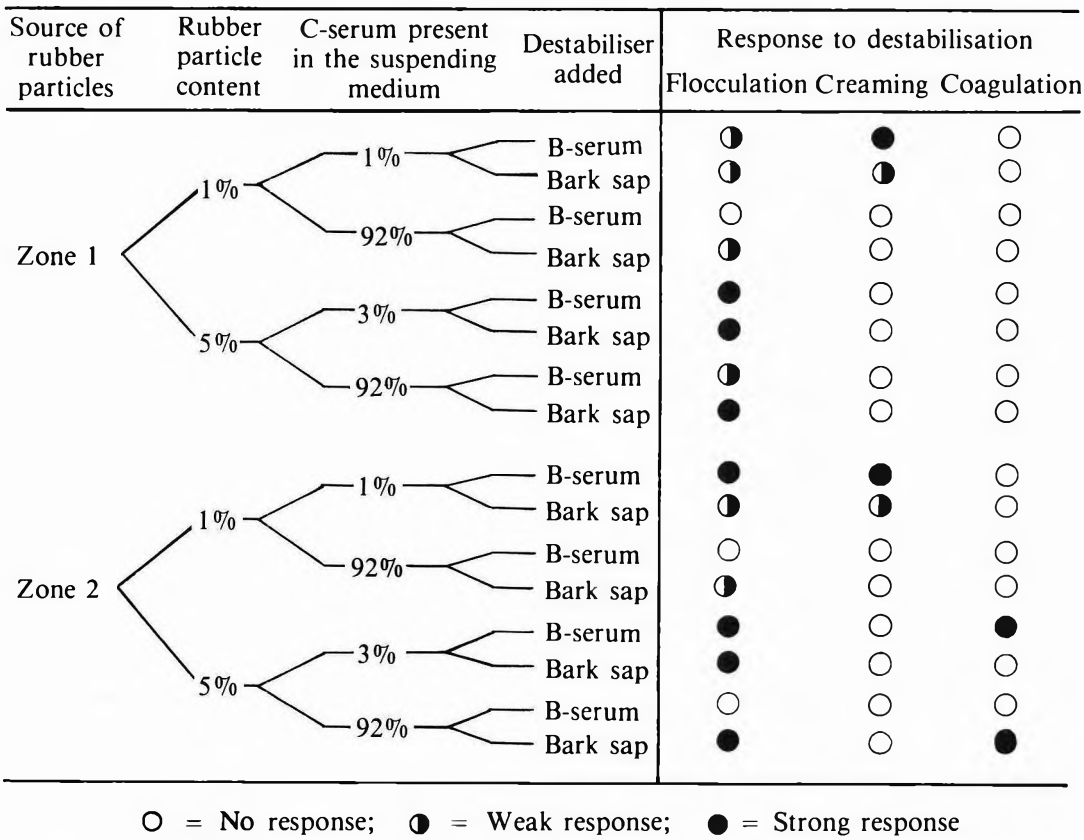

Figure 5. Summary of the destabilising responses in rubber particle suspensions in relation to the source of the rubber particles, the rubber particle content, the substantial presence or absence of C-serum and the destabiliser used.

Among the three responses to destabilisation — flocculation, creaming and coagulation — creaming could least be likened to the destabilisation of whole latex. It occurred only when both the rubber particle and the C-serum content were extremely low: conditions that are not readily met *in vivo*. (Nevertheless, this does not preclude creaming from being usefully employed as an indicator of destabilisation.)

Rubber particle flocculation was the response most readily induced and under appropriate experimental conditions, floc formation was instantaneous upon addition of the destabiliser. The rapidity of the response was consistent with a possible role in latex vessel plugging. While small amounts of microscopic flocs are always present in collected latex[6], the flocs described in this report were visible to the unaided eye. They were therefore more than adequate in size to obstruct latex vessels in the formation of plugs or in tree dryness even without their coalescing to form a coagulum.

Coagulation of rubber particles requires first the adhesion of the particles to one another (flocculation) and, additionally, the lysis of rubber particle membranes to enable coalescence of the particles. It was observed that the degree of flocculation did not always correspond with the extent of coagulation. While coagulation was usually preceded by flocculation, the latter often took place without subsequent coagulation. For example, bark sap induced copious flocculation in a suspension of 5% *Zone 2* rubber particles in the relative absence of C-serum. But unless C-serum was also included in the suspension, coagulation did not occur *(Figure 3)*. This observation points to the existence of an essential factor present in C-serum that triggered coagulum formation in rubber particle suspensions destabilised by bark sap. A putative enzyme, 'coagulase', with rubber coagulating properties has been reported in C-serum[14,15], but it was effective in coagulating only heated rubber particles in the presence of added calcium. Its relevance to the coagulation reaction in the present study is therefore doubtful.

When coagulation was induced by B-serum, the presence of C-serum was not required. Indeed, C-serum strongly inhibited the coagulation response (the same also being true of the other two destabilising responses, flocculation and creaming). The striking difference in C-serum requirement for the coagulation response suggests a possible dissimilarity in the modes of action of B-serum and bark sap in coagulating rubber particles. This needs to be ascertained. The ability of the cationic B-serum to nullify the electrostatic stability of the negatively charged rubber particles has been reported[7]. In this connection, it is comprehensible how C-serum (which has a net negative charge) is antagonistic to B-serum and deemed to have a 'protective' effect on rubber particles against the destabilising effect of B-serum[6,7]. The same line of reasoning is obviously inapplicable to bark sap activity where C-serum contributes to coagulation rather than inhibits it. The mode of action of the largely anionic bark sap has yet to be determined.

The results from this study showed a marked difference in the susceptibility to destabilisation between the larger, low density rubber particles of *Zone 1* (which accounts for the major proportion of rubber in the latex) and the smaller, high density particles (which are the main constituents of *Zones 2* and *3* of centrifuged latex). Not only were the high density rubber particles more sensitive to destabilisation induced by bark sap as previously noted[12], but this was also the case when destabilisation was induced by B-serum. Coagulation occurred only with the *Zone 2* rubber particles and generally these particles also tended to flocculate more readily than those from *Zone 1*. Among the rubber particle destabilisation responses, only in the creaming reaction did *Zone 1* particles fare better. Even then, this could be due largely to the lower density of the *Zone 1* particles which enhanced their floatation to form a cream.

The destabilisation responses in the rubber particle suspensions observed in this investigation enables a conceptualisation of how destabilisation might occur in whole latex. (One disadvantage of using whole latex in the experiments is that the amount of B-serum in the test mixtures cannot be controlled accurately;

lutoids present in latex are liable to rupture with the consequent release of more B-serum.) The results from this study suggest that the physiological processes in latex destabilisation that could be concerned with latex plug formation and in tree dryness involve the following:

- *Rubber particles,* those from *Zone 2* of centrifuged latex (*i.e.* the high-density particles) being especially sensitive to flocculation and coagulation
- *B-serum* which has strong rubber particle destabilising activity (flocculation, creaming and coagulation) only when the ambient C-serum concentration is low
- *Bark sap* which induces rubber particle flocculation and coagulation in the presence of C-serum and induces flocculation in its absence
- *C-serum* which strongly inhibits the destabilising activity of B-serum but not of bark sap to which it supplies a coagulation-inducing factor.

It appears probable that B-serum and bark sap complement each other in the induction of latex instability, the relative activity of either destabiliser being dependent partly on their availability at the reaction site and on the ambient C-serum present. Whichever destabiliser is involved, the smaller, high-density rubber particles in latex are especially susceptible to destabilisation. As suggested previously[12], these particles, when sensitised to instability, might serve as nuclei in the agglomeration of destabilised rubber particles leading to the formation of latex vessel plugs. A similar phenomenon might take place within the latex vessels of trees with incipient dryness, resulting in the coagulation of rubber within the vessels eventually.

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REFERENCES

1. BOATMAN, S.G. (1966) Preliminary Physiological Studies on the Promotion of Latex Flow by Plant Growth Regulators. *J. Rubb. Res. Inst. Malaya,* **19(5),** 243.
2. SOUTHORN, W.A. (1969) Physiology of *Hevea* (Latex Flow). *J. Rubb. Res. Inst. Malaya,* **21(4),** 494.
3. GOMEZ, J.B. (1983) Physiology of Latex (Rubber) Production. *M.R.R.D.B. Monogr. No. 8.* Kuala Lumpur: Malaysian Rubber Research and Development Board.
4. SOUTHORN, W.A. (1968) Latex Flow Studies. I. Electron Microscopy of *Hevea brasiliensis* in the Region of the Tapping Cut. *J. Rubb. Res. Inst. Malaya,* **20(4),** 176.
5. PARANJOTHY, K., GOMEZ, J.B. AND YEANG, H.Y. (1976) Physiological Aspects of Brown Bast Development. *Proc. Int. Rubb. Conf. 1975 Kuala Lumpur,* **2,** 181.
6. SOUTHORN, W.A. AND EDWIN, E.E. (1968) Latex Flow Studies. II. Influence of Lutoids on the Stability and Flow of *Hevea* Latex. *J. Rubb. Res. Inst. Malaya,* **20(4),** 187.
7. SOUTHORN, W.A. AND YIP, E. (1968) Latex Flow Studies. III. Electrostatic Considerations in the Colloidal Stability of Fresh *Hevea* Latex. *J. Rubb. Res. Inst. Malaya,* **20(4),** 201.
8. YIP, E. AND SOUTHORN, W.A. (1968) Latex Flow Studies. VI. Effects of High Pressure Gradients on Flow of Fresh *Hevea* Latex in Narrow Bore Capillaries. *J. Rubb. Res. Inst. Malaya,* **20(5),** 248.
9. GOMEZ, J.B. (1977) Demonstration of Latex Coagulants in Bark Extracts of *Hevea* and Their Possible Role in Latex Flow. *J. Rubb. Res. Inst. Malaysia,* **25(3),** 109.
10. YIP, E. AND GOMEZ, J.B. (1984) Characterisation of Cell Sap of *Hevea* and Its Influence on Cessation of Latex Flow. *J. Rubb. Res. Inst. Malaysia,* **32(1),** 1.
11. YEANG, H.Y. (1986) Latex De-stabilisation by Coagulants in *Hevea* Bark. *Proc. IRRDB Rubb. Physiology and Exploitation Meet. 1986, SCATC, Hainan, China,* 75.
12. YEANG, H.Y. (1988) Destabilisation of *Hevea* Latex by Bark Sap: Involvement of High Density Rubber Particles in the Latex. *J. nat. Rubb. Res.,* **3(2),** 115.
13. MOIR, G.F.J. (1959) Ultracentrifugation and Staining of *Hevea* Latex. *Nature, Lond.,* **184(4699),** 1926.
14. WOO, C.H. (1973) Rubber Coagulation by Enzymes of *Hevea brasiliensis* Latex. *J. Rubb. Res. Inst. Malaya,* **23(5),** 323.
15. WOO, C.H. (1976) 'Coagulase' from the Fractionation of C-serum of *Hevea* Latex. *J. Rubb. Res. Inst. Malaysia,* **24(4),** 227.

J. nat. Rubb. Res., **4(1)**, 56-65

Lesion Size, Latent Period and Sporulation on Leaf Discs as Indicators of Resistance of Hevea *to* Microcyclus ulei

ISMAIL HASHIM* AND J.C.R. PEREIRA**

There were clonal differences in the rate of development of mycelium and appearance of lesions, sizes of lesions, latent period and the quantity of conidia produced on discs of Hevea *leaves. There was a positive correlation between conidial production and lesion size, and negative correlations existed between conidial production and latent period and lesion size and latent period. Latent period and sporulation are also important components for assessment of resistance.*

Clones GT 711, RRIM 501, CNS AM 7701, SIAL 842 and SIAL 263 possessed relatively smaller lesions, longer latent periods and reduced sporulation. On these clones, the differences in lesion size were significant between clones but not between races of Microcyclus ulei. *However, differences in conidial production between clones, races and the interaction between clones and races were significant.*

In earlier programmes to breed *Hevea* clones resistant to South American leaf blight (SALB) caused by *Microcyclus ulei* (P. Henn.) v. Arx, crosses were made mostly between high-yielding oriental clones and South American clones, or their hybrids which are highly resistant if not immune to some races of *M. ulei*[1-4]. Most of the resistant off-springs of these crosses are resistant to some races of *M. ulei,* hence their resistance is race-specific. Since many races of *M. ulei* had been identified[5-7], and vertical resistance had failed[8], breeding for horizontal resistance to SALB is encouraged[6,8].

In many other diseases, the components of resistance often associated with horizontal resistance are low infection frequency, long incubation and/or latent period and reduced sporulation[9-18]. In the case of *Hevea,* resistant clones have been reported to produce less spores when infected with *M. ulei*[19]. It was also observed that lesions took a longer time to develop on resistant clones than on susceptible clones[20]. Clonal variations in number and size of lesions as well as conidial production have been recorded[1,20-22].

Hevea rubber is a perennial tree crop which can benefit from a laboratory method of screening resistance. One of the advantages of a laboratory method is that it offers the possibility of controlling climatic conditions which are known to affect the level of horizontal resistance[15]. A drawback is that laboratory results may not correspond with resistance of mature plants in the field. However, laboratory and glass-house results can be useful if carefully related to field results[8]. For example, laboratory methods were used to evaluate the resistance of lettuce to mildew[15] and coffee to leaf rust and berry disease[23]. Similarly, Chee[1] had correlated sizes of lesions on leaf discs with resistance of nursery plants to *M. ulei.* This study investigated lesion sizes, latent periods and sporulation of leaf discs as indicators of resistance of *Hevea* to *M. ulei.*

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MATERIALS AND METHODS

Inoculum and Plant Materials

Conidia obtained from infected leaves harvested from EDJAB Station, Una, Bahia were used in trials where field conidia were the inoculum. When a definite race of *M. ulei* was required, conidia were obtained from pure cultures. For this purpose, the cultures were grown on potato sucrose agar amended with Panvit^{R} (a mixture of vitamins, minerals and amino acids) and Bonzo^{R} dogfood[24], incubated and light-conditioned to induce sporulation as described previously[7].

Leaves were obtained from the same station. *Hevea* clones used in this study were FX 4163, FX 985, FX 3846, FX 3864, FX 2261, FX 2804, FX 3844, FX 25, IAN 717, IAN 710, IAN 713, RRIM 600, RRIM 501, MDF 180, CNS AM 7808, CNS AM 7701, SIAL 263, SIAL 842, CA 255, GT 711 and PA 31.

Inoculation of Leaf Discs

Leaf discs cut from young *Hevea* leaves (about seven days old) were floated on distilled water in petri dishes and sprayed with a suspension of conidia (1×10^5 conidia/ml) as mentioned previously[1]. Subsequently, the dishes were incubated at 24°C under continuous light in an incubator.

Assessment of Resistance

Mycelial development. Leaf discs, 48 h after being inoculated, were submerged for 24 h in a solution containing 100 ml ethyl alcohol (95%), 25 ml lactophenol, 75 ml chloral hydrate (2 g/ml) and 0.4 g cotton blue. The discs were washed with distilled water and cleared in a solution of chloral hydrate (2 g/ml). Cleared discs were mounted in glycerine on glass slides.

Mycelial development was rated into three categories: *A*, conidia germinated with short germtube, no penetration; *B*, conidia germinated and the mycelium had penetrated into the leaf tissues, however mycelial branching was absent or minimal; *C*, the conidia were associated with long and branching mycelia.

Rate of appearance of lesions. The rate of appearance of lesions was determined for eight clones: IAN 717, FX 2261, FX 2804, FX 985, FX 3864, FX 4163, FX 3844 and FX 25. For clones IAN 717, FX 2261 and FX 2804, they were inoculated with field conidia obtained from these same clones respectively. Other clones were inoculated with conidia from clone FX 985. The number of lesions appeared was counted five, six and seven days after inoculation.

Size of lesions. Unless otherwise stated, the size of lesions was determined six days after inoculation by using a dot scale[25].

Latent period. Latent period is the interval (days) between inoculation and the day sporulation is first detected.

Sporulation. The conidia were harvested at definite intervals after inoculation as mentioned in the *Results* by agitating the leaf discs in 3 ml, 5 ml or 10 ml of distilled water containing a drop of diluted Triton × 114. A haemocytometer was used to determine the concentration of conidia.

RESULTS

Mycelial Development

Microscopic observations of cleared leaf discs indicated that conidial germination and mycelial penetration into the leaf tissues occurred for both the compatible (lesion formed) and incompatible (no lesion formed) host-pathogen combinations *(Table 1)*. When the rate of mycelial development was estimated at 48 h after inoculation, the growth of mycelium in the leaf discs was more advanced in the compatible host-pathogen combinations compared to the incompatible combinations as the percentage of conidia which had reached *Category C* rating of fungal development was higher for the compatible than in the incompatible combinations (*Tables 1* and *2*). In the incompatible combinations, fungal development ceased to progress following penetrations as indicated by the greater percentage of conidia still in *Category B (Table 2)*. Among the compatible host-parasite combinations, mycelium development was slower in clone FX 3864 *(Table 1)*.

TABLE 1. DEVELOPMENT OF *MICROCYCLUS ULEI* ON LEAF DISCS OF *HEVEA* 48 H AFTER INOCULATION

Test clone	Source of conidia	Percentage number of conidia with fungal development rating			Lesion formation
		A	B	C	
FX 985	FX 2804	30.80	69.20	0.00	–
	FX 2261	30.80	57.55	11.65	–
	FX 985	4.15	14.85	80.80	+
FX 2261	FX 2804	45.00	45.00	10.00	–
	FX 2261	14.20	23.30	62.50	+
	FX 985	30.80	64.20	5.00	–
FX 3864	FX 2804	23.35	46.65	30.00	+
	FX 2261	22.50	15.83	45.85	+
	FX 985	13.35	36.65	50.00	+
IAN 717	FX 2804	3.30	6.35	90.35	+
	FX 2261	40.00	45.85	14.15	–
	FX 985	24.20	27.00	48.30	–
PA 31	FX 2804	17.50	79.15	3.35	–
	FX 2261	35.85	64.15	0.00	–
	FX 985	30.85	67.45	1.70	–

Data are averages of two experiments and sixty germinated conidia were observed per experiment

For fungal development rating, *see Methods.*

Lesion formation: –, no lesion formed: +, lesion formed

The conidia from FX 2804, FX 2261 and FX 985 were *Races 2, 4* and *6* respectively.

Rate of Appearance of Lesions

The rate of appearance of lesions on leaf discs of eight *Hevea* clones, which is an indication of the incubation period, is shown in *Table 3*. On these clones, lesions were obviously visible on the fifth day after inoculation. The increase in the number of lesions was greatest between the fifth and the sixth day while the difference occurring between the sixth and seventh day was small *(Table 3)*. When the number of lesions developed by *Day 5* expressed as a percentage to that of *Day 7* was compared between clones, there was no significant differences between most clones except for clone FX 2261 which showed a significantly lower percentage compared to the other clones. This indicated that the incubation period was longer on clone FX 2261. Similar results were obtained when the number of lesions developed by *Day 6* was expressed as a percentage of the number of *Day 7 (Table 3)*.

TABLE 2. DEVELOPMENT OF COMPATIBLE AND INCOMPATIBLE RACES OF *MICROCYCLUS ULEI* ON *HEVEA* LEAF DISCS

Compatibility[a]	Percentage number of conidia with fungal development rating[b]		
	A	B	C
Compatible	13.48	26.66	61.25
Incompatible	31.76	57.73	10.46
	$p < 0.005$	$p < 0.005$	$p < 0.005$

[a] *See Table 1*, compatible combinations were when lesions formed.

[b] The rating of fungal development is given in *Methods*.

TABLE 3. APPEARANCE OF LESIONS ON LEAF DISCS OF EIGHT *HEVEA* CLONES INOCULATED WITH *MICROCYCLUS ULEI*

Clone	No. (mean) of lesions			Lesion number of Day 5 or Day 6 as % (mean) of Day 7	
	Day 5	Day 6	Day 7	Day 5	Day 6
FX 2261	9.75	22.28	40.80	22.97 (2.9)	52.53 (6.4)
IAN 717	29.72	46.48	57.58	51.25 (2.3)	83.77 (3.1)
FX 985	37.92	61.12	74.18	50.42 (7.5)	82.93 (1.9)
FX 2804	31.13	61.57	67.57	40.90 (7.6)	89.24 (4.3)
FX 3864	31.45	56.18	62.23	49.35 (5.9)	89.98 (2.4)
FX 4163	32.25	62.48	67.68	52.15 (5.3)	92.96 (2.5)
FX 3844	33.15	63.62	72.33	42.21 (5.1)	87.01 (4.2)
FX 25	40.50	81.37	100.12	39.38 (4.1)	81.92 (4.3)
		F		3.98**	0.76^{NS}
		$L.S.D._{0.05}$		13.95	17.87
		C.V. (%)		27.43	18.48

Analysis of variance indicated significance at 1% (**) or non-significance (NS).
Numbers within brackets are standard errors.

Lesion Size

There is a large clonal variation in the size of lesions developed on *Hevea* leaf discs inoculated with conidia of *M. ulei (Figure 1).* Clones MDF 180, FX 4163 and FX 3864 produced larger lesions while the lesions on clones GT 711, RRIM 501, CNS AM 7701 and SIAL 842 were smaller.

The sizes of lesions on six selected *Hevea* clones inoculated with three races of *M. ulei* are shown in *Table 4.* No lesion was observed on FX 985 and SIAL 842 inoculated with *Race 2.* The sizes of lesions developed on these clones indicated significant differences ($p = 0.01$) between clones, however the differences between races were not significant. The clone × race interaction was also not significant.

Latent Period

The length of the latent period of various clones is shown in *Figure 1.* On leaf discs, conidia were detected six days after inoculation of some clones while the latent period was longer on clone GT 711 (eleven days), RRIM 501 (thirteen days), and fourteen days for clones SIAL 842 and CNS AM 7701.

There was a negative correlation ($r = -0.86$) between lesion size and latent period *(Figure 1).* Generally, clones with smaller lesions had longer latent periods. However, some clones (FX 985, FX3846, FX 2261, IAN 717, FX 2804, CNS AM 7808, IAN 710, FX 25 and RRIM 513) possessing about similar sizes of lesions had a wider variation of latent periods varying from six to eleven days *(Figure 1).*

Sporulation

The amount of conidia produced on leaf discs varied with the clones *(Figure 2).* Sporulation was high on clones FX 4163, FX 985 and FX 3846 and very low on clones GT 711, RRIM 501, CNS AM 7701 and SIAL 842. Sporulation was influenced by sizes of lesions and latent period. There was a negative correlation ($r = -0.717$) between the quantity of conidia produced and latent period *(Figure 2),* and a positive correlation ($r = 0.643$) between lesion size and the amount of conidia produced *(Figure 3).* Clones such as FX 25, FX 3864,

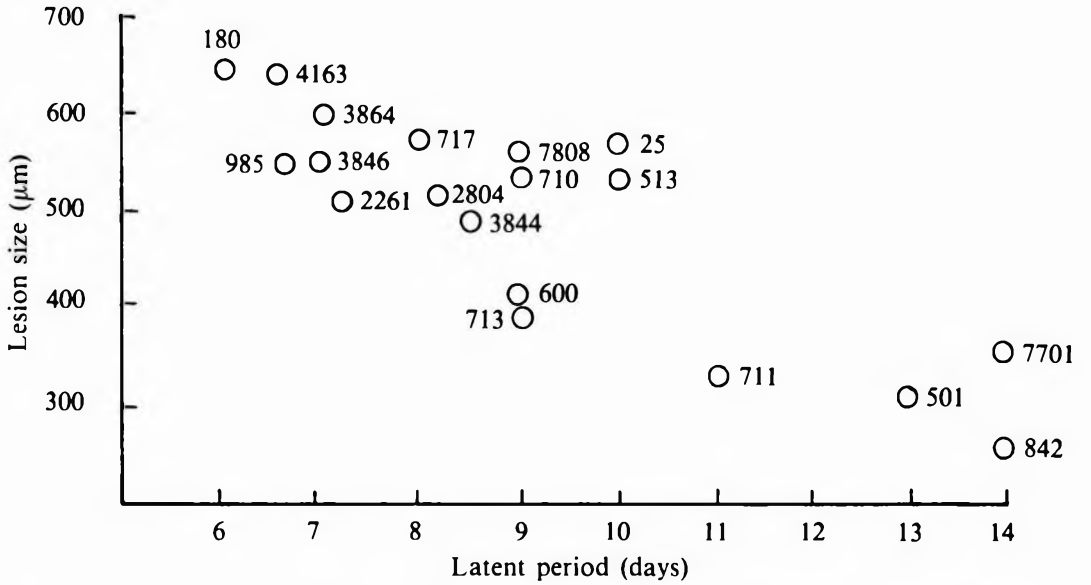

Figure 1. Relationship between lesion size and latent period on leaf discs of different Hevea *clones inoculated with* M. ulei.

TABLE 4. LESION SIZE AND SPORULATION ON LEAF DISCS OF SIX *HEVEA* CLONES INOCULATED WITH THREE RACES OF *MICROCYCLUS ULEI*

Clone	Mean size of lesion (μm)				Conidia produced/disc ($\times 10^4$)[a]			
	Race 2	Race 5	Race 6	Mean	Race 2	Race 5	Race 6	Mean
SIAL 263	363.0	263.3	341.7	322.8	5.32	2.12	1.89	3.11
GT 711	288.7	303.3	317.0	303.0	4.26	4.19	3.06	3.84
RRIM 501	200.0	272.0	249.0	240.3	0.21	2.71	0.58	1.17
SIAL 842	NL	227.7	231.0	229.4	0.00	0.64	0.24	0.29
FX 985	NL	449.0	427.7	438.5	0.00	23.47	4.33	9.27
CNS AM 7701	200.0	254.3	212.7	222.3	0.14	0.39	0.15	0.23
Mean	175.3	294.9	296.5		1.66	5.59	1.71	
Analysis of variance								
Source	df	MS		p	df	MS		p
Replicate	2	118.74		NS	2	2.3615		NS
Clone	5	35 955.35		**	5	104.8580		**
Error (a)	10	458.56			10	0.9371		
Race	2	87 052.07		NS	2	91.9335		*
Race × clone	10	34 674.69		NS	10	78.8521		**
Error (b)	24	30 137.88			24	1.1175		

NS = Not significant; *Significant at $P<0.05$; **Significant at $P<0.01$

NL = No lesion formed

[a]Conidia were harvested nine days after inoculation for clone FX 985 and fourteen days after inoculation for the other clones.

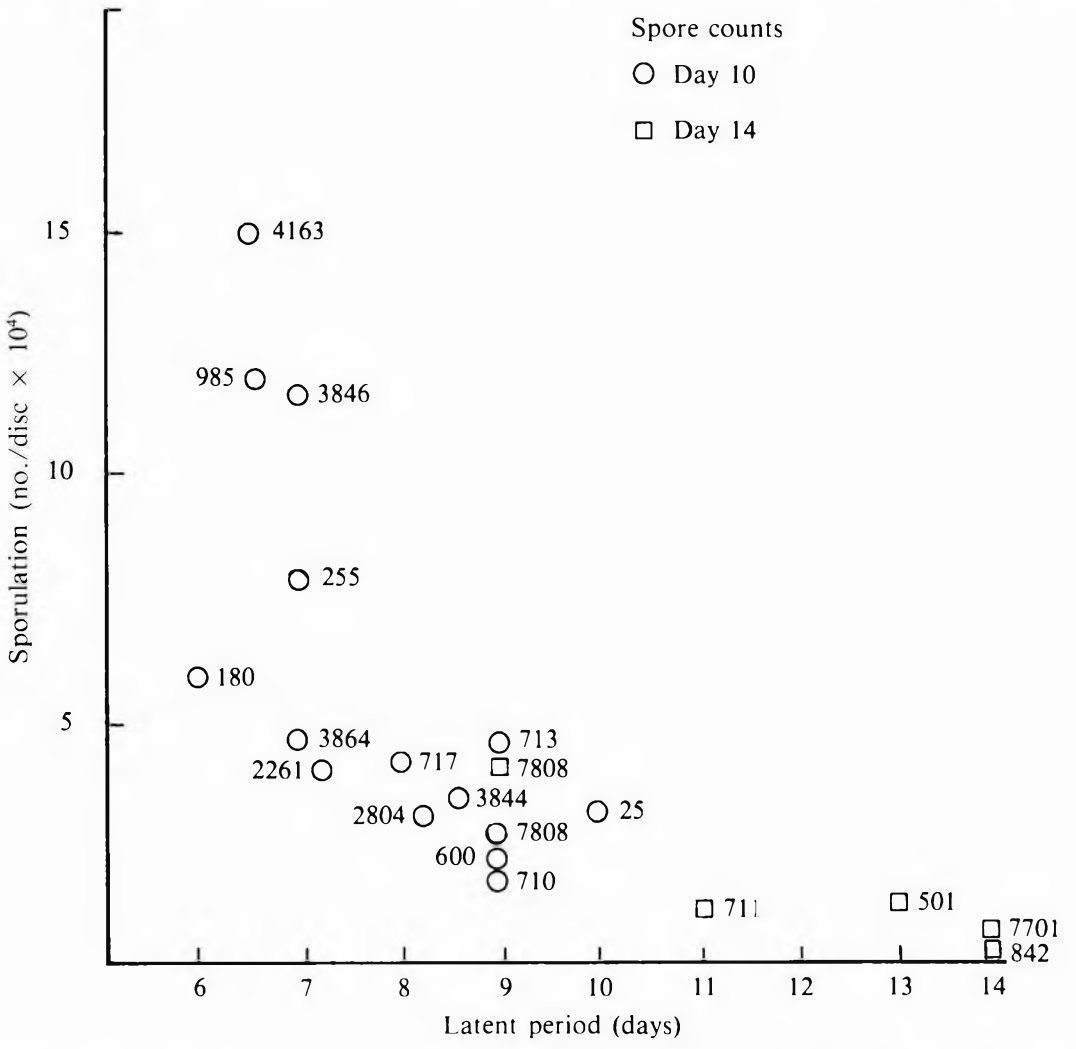

Figure 2. Relationship between latent period and sporulation of M. ulei *on leaf discs of different* Hevea *clones. Spore counts were done on* Day 10 *or* Day 14 *after inoculation.*

MDF 180 and CNS AM 7808 produced large lesions; however, the amount of conidia produced was low *(Figure 3)*. Similarly, results shown in *Table 5* indicated that clones with slight variation in the sizes of lesions, indicated significant differences when the amount of conidia produced was determined. In fact, the sizes of lesions on clones such as FX 2261, FX 2804 and FX 3844 were smaller than on clone FX 25; however, the amounts of conidia produced on these clones were greater than on FX 25 *(Table 5)*.

The amounts of conidia produced on six selected clones inoculated with three races of *M. ulei* are shown in *Table 4*. The amount of conidia produced showed significant differences both between clones and between races. The interaction between clone and race was also significant.

DISCUSSION

Parlevliet[10] stated that often there was no resistance to infection, germination, appressorium formation and penetration by bio-

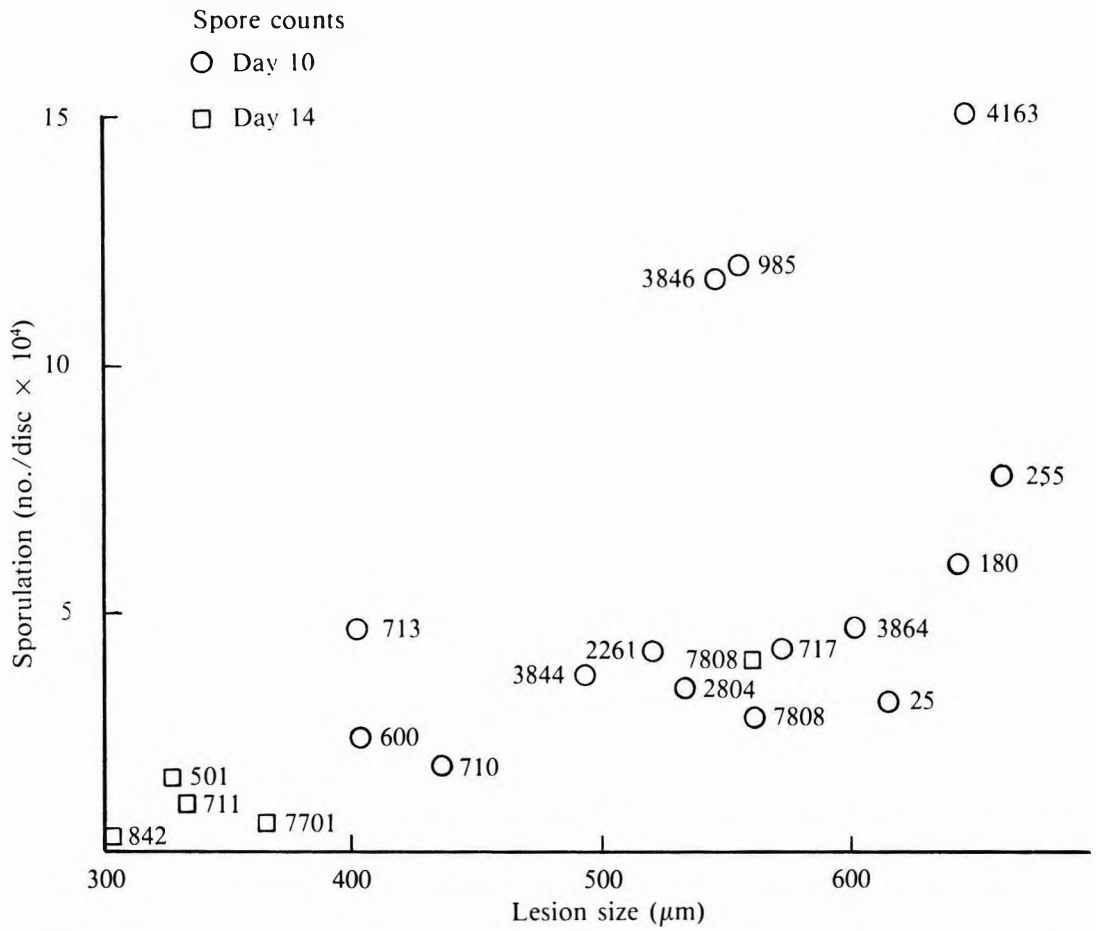

Figure 3. Relationship between lesion size and sporulation of M. ulei *on leaf discs of different* Hevea *clones.*

trophic pathogens. In conformity, this study confirms an earlier observation[26] that conidial germination and mycelial penetration occurred on all clones tested irrespective of their resistance. However, no fungal development occurred beyond penetration and slight mycelial growth in incompatible host-parasite combinations *(Table 1)*. This suggests that in order to assess varietal resistance of *Hevea* to *M. ulei,* fungal development beyond penetration of the epidermal layer needs to be compared.

Inoculation of leaf discs is useful in determining the occurrence of vertical resistance *(Table 1),* and it could also measure the quantitative resistance in disease resistance especially when latent period and sporulation were considered. Earlier, Chee[1] assessed resistance of *Hevea* to *M. ulei* in the laboratory by measuring only the sizes of lesions on leaf discs. The present study indicated that generally the clonal variations between lesion size, latent period and sporulation were associated. A higher correlation existed between lesion size and latent period as both components measure the rate of growth of mycelium in the host tissues. In addition, Johnson and Taylor[9] considered that resistance to growth of mycelium and resistance to production of spores could also be closely related. However, there were exceptions in these relationships. Some *Hevea* clones which developed larger lesions had longer latent

TABLE 5. PRODUCTION OF CONIDIA ON LEAF DISCS OF *HEVEA* INOCULATED WITH *MICROCYCLUS ULEI*

Clone	Lesion size (μm)	Latent period (days)	Conidia harvested on Day 9			Conidia harvested on Day 11		
			No./disc ($\times 10^4$)	No./lesion ($\times 10^2$)	No./lesion/ day ($\times 10^2$)	No./disc ($\times 10^4$)	No./lesion ($\times 10^2$)	No./lesion/ day ($\times 10^2$)
FX 2261	509	7–9	4.12 (2.2)	8.79 (3.7)	6.27 (2.1)	10.09 (1.0	23.73 (1.6)	5.93 (0.4)
FX 2804	515	7–9	3.27 (0.3)	4.43 (0.6)	3.48 (0.4)	3.72 (0.7)	5.12 (0.9)	2.56 (0.5)
IAN 717	569	8–9	4.24 (1.0)	5.62 (1.0)	5.62 (1.0)	—	—	—
FX 985	549	6–7	12.37 (1.1)	14.45 (1.7)	5.76 (1.4)	9.23 (2.3)	14.49 (2.4)	3.62 (0.6)
FX 3864	599	7–8	4.72 (0.6)	8.11 (1.5)	4.06 (0.7)	6.26 (0.5)	8.81 (0.4)	2.20 (0.1)
FX 4163	641	6–7	15.31 (2.7)	17.37 (0.9)	6.68 (0.7)	16.46 (8.3)	27.29 (4.0)	6.25 (0.5)
FX 3844	489	7–9	3.57 (0.7)	3.97 (1.0)	3.12 (0.8)	1.63 (0.3)	1.95 (0.1)	0.98 (0.1)
FX 25	573	9–11	0.42 (0.1)	0.41 (0.1)	0.41 (0.1)	0.70 (0.4)	0.66 (0.4)	0.66 (0.4)
F			13.86**	11.72**	3.86*	2.26^{NS}	24.70***	27.66***
$L.S.D._{0.05}$			4.09	4.93	3.19	10.84	6.07	1.20

Numbers within brackets are standard errors.

Analysis of variance indicated significance at 5% (*), 1% (**), 0.1% (***) or non-significance (NS)

– = No data

periods and sporulated poorly. Thus latent period and sporulation, the components of resistance which are commonly determined to assess for horizontal resistance in other diseases[9-18], should also be considered when clones of *Hevea* are assessed for resistance, especially horizontal resistance. After all, Langford[20] observed that complete or partial inhibition of sporulation of *M. ulei* on *Hevea* is an expression of resistance as consistent as resistance to leaf damage and defoliation and hence suggested that sporulation should be given even or greater merit in the selection of *Hevea* clones for resistance to *M. ulei.* In other diseases[9,17,18], sporulation is considered a more sensitive component of resistance to diseases. Sporulation is also a sensitive test for differential interaction with races of a pathogen which is often due to race specific resistance[9]. This is clearly shown in *Table 4* where the clonal interaction with races of *M. ulei* was not significant when lesion size was analysed while the interaction was significant when sporulation was considered. Moreover, clones with slight variation in lesion size possessed greater differences in conidia production *(Table 5)* and latent period *(Figure 1).*

When resistance of *Hevea* to *M. ulei* was assessed in the laboratory, determination of the latent period and amount of conidia produced enhanced the reliability of measuring only lesion size especially when horizontal resistance was selected. Inoculation of leaf discs or probably a detached leaf is a useful tool in the early selection of clones for resistance, even for horizontal resistance.

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REFERENCES

1. CHEE, K.H. (1976) Assessing Susceptibility of *Hevea* Clones to *Microcyclus ulei. Ann. appl. Biol.,* **84,** 135.

2. BOS, H. AND MCINDOE, K.G. (1965) Breeding of *Hevea* for Resistance against *Dothidella ulei. J. Rubb. Res. Inst. Malaya,* **19(2),** 98.

3. GONCALVES, J.R.C. (1968) The Resistance of FX and IAN Rubber Clones to Leaf Diseases in Brasil. *Trop. Agric. Trin.,* **45,** 331.

4. GONCALVES, J.R.C. (1970) Resistance de Clones de Seringueira Provenientes do Brasil e da America Central a Isolars de *Dothidella ulei* sob Condicoes de Casa de Vidro. *Inst. Pesq. Exp. Agropecuarias, Fitotecnia,* **4,** 27.

5. MILLER, J.W. (1966) Differential Clones of *Hevea* for Identifying Races of *Dothidella ulei. Pl. Dis. Rep.,* **50,** 187.

6. CHEE, K.H., ZHANG, K.M. AND DARMONO, T.W. (1986) The Occurrence of Eight Races of *Microcyclus ulei* on *Hevea* Rubber in Bahia, Brasil. *Trans. Br. mycol. Soc.,* **87,** 15.

7. HASHIM, I. AND ALMEIDA, L.C.C. (1987) Identification of Races and *in vitro* Sporulation of *Microcyclus ulei. J. nat. Rubb. Res.,* **2(2),** 111.

8. SIMMONDS, N.W. (1986) Strategies for Disease Resistance Breeding in Tropical Perennial Crops. *Breeding for Durable Resistance in Perennial Crops.* FAO Plant Production and Protection Paper 70, 3.

9. JOHNSON, R. AND TAYLOR, A.J. (1976) Spore Yield of Pathogens in the Investigation of Race Specificity of Host Resistance. *Ann. Rev. Phytopathol.,* **14,** 97.

10. PARLEVLIET, J.E. (1979) Components of Resistance that Reduce the Rate of Epidemic Development. *Ann. Rev. Phytopathol.,* **17,** 203.

11. ROUSE, A.I., NELSON, R.R., MACKENZIE, D.R. AND ARMITAGE, C.R. (1980) Components of Rate Reducing Resistance in Seedlings of Four Wheat Cultivars and Parasitic Fitness in Six Isolates of *Erisiphe graminis* f. sp. tritici. *Phytopathology,* **70,** 1097.

12. ASHER, M.J.C. AND THOMAS, C.E. (1984) Components of Partial Resistance to *Erisiphe graminis* in Spring Barley. *Pl. Pathol.,* **33,** 123.

13. NEERVOORT, W.J. AND PARLEVLIET, J.E. (1978) Partial Resistance of Barley to Leaf Rust, *Puccinia hordei.* V. Analysis of the Components of Partial Resistance in Eight Barley Cultivars. *Euphytica,* **27,** 33.

14. PARLEVLIET, J.E. AND VAN OMMEREN, A. (1975) Partial Resistance of Barley to Leaf Rust. II. Relationship between Field Trials, Microplot Tests and Latent Period. *Euphytica,* **24,** 293.

15. EENINK, A.H. AND DEJONG, C.V. (1982) Partial Resistance of Lettuce to Downy Mildew. 3. Correspondence between Resistance Levels of Cotyledons and Leaf Discs and Resistance of Adult Plants. *Euphytica,* **31,** 761.

16. LANCASHIRE, P.D. AND GARETH, J.D. (1985) Components of Partial Resistance to *Septoria nodurum* in Winter Wheat. *Ann. appl. Biol.*, **106**, 541.

17. LAPWOOD, D.H. (1961) Potato Haulm Resistance to *Phytophthora infestans*. II. Lesion Production and Sporulation. *Ann. appl. Biol.*, **49**, 316.

18. HABGOOD, R.M. (1977) Resistance of Barley Cultivars to *Rhynchosporium secalis*. *Trans. Br. mycol. Soc.*, **69**, 281.

19. NEWSAM, A. (1968) Pathological Division. *Rep. Rubb. Res. Inst. Malaysia 1967*, 62.

20. LANGFORD, M.H. (1945) South American Leaf Blight of *Hevea* Rubber Trees. *Tech. Bull. United States Department of Agriculture No. 882.*

21. CHEE, K.H., DARMONO, T.W., ZHANG, K.M. AND LIEBEREI, R. (1985) Leaf Development, and Spore Production and Germination after Infection of *Hevea* Leaves by *Microcyclus ulei*. *J. Rubb. Res. Inst. Malaysia*, **33(3)**, 124.

22. JUNQUEIRA, N.T.V. (1985) Variabilidade Fisiologica de *Microcyclus ulei*. Ph.D. Thesis, University Federal Vicosa, Brasil.

23. VAN DER GRAAF, N.A. (1986) Coffees, *Coffea* spp. *Breeding for Durable Resistance in Perennial Crops*. FAO Plant Production and Protection Paper 70, 49.

24. JUNQUEIRA, N.T.V., CHAVES, G.M., ZAMBOLIM, L., ROMEIRO, R.S. AND GASPOROTTO, L. (1984) Isolamento, Cultivo e Esporulacao de *Microcyclus ulei*, Agente Etilogico do Mal das Folhas da Seringueira. *Revta. Ceres*, **31**, 322.

25. DARMONO, T.W. AND CHEE, K.H. (1985) Reaction of *Hevea* Clones to Races of *Microcyclus ulei* in Brasil. *J. Rubb. Res. Inst. Malaysia*, **33(1)**, 1.

26. HASHIM, I., CHEE, K.H. AND DUNCAN, E.J. (1978) Reaction of *Hevea* Leaves to Infection with *Microcyclus ulei*. *J. Rubb. Res. Inst. Malaysia*, **26(1)**, 67.

J. nat. Rubb. Res., **4(1)**, 66–74

Effects of Selected Environmental and Technological Factors on Rubber Production — A Case Study of RRIM Economic Laboratory

MOHD. NAPI DAUD*, JAMES NAYAGAM* AND P. VERAMUTHOO*

Production of rubber in a certain locality is dependent on a number of biological, environmental and technological factors. In this paper, the effects of selected environmental and technological factors such as rainfall, tapping days, wintering, improved tapping technique and yield stimulation on production in the RRIM Economic Laboratory at Kota Tinggi, Johore Darul Takzim were studied. The data covered a twelve-year period.

The analyses were done in two stages. In the first stage, the effects of diurnal and monthly variations of rainfall on output were assessed; whereas in the second stage, the Cobb-Douglas production model was used to measure the combined effects of environmental and technological factors on production.

The findings showed that the wettest months were October to January which were also the highest yielding months and, thus, losses in potential crop due to rain interference in these months were substantial. The regression analysis showed that all variables used in the model except stimulation dummy were significant at $P<0.05$. These variables explained approximately 62% of the total variation in the prodction of rubber in the RRIM Economic Laboratory.

The amount of rubber output obtained from given high-yielding cultivars in a locality is dependent on a number of environmental and technological factors. Of the environmental factors weather conditions, particularly the time and amount of rainfall, have adverse effects on output. Occurrence of rainfall during the normal working hours when tapping is carried out usually disrupts or prevents the harvesting of latex, thus affecting the quantity and quality of latex collected[1]. A higher number of rainy days during a period decreases yield, and rainfall intensity beyond 10–11 mm rain per rainy day is not congenial to high yields[2]. On the other hand, improved techniques of tapping and the periodical application of yield stimulants increase the output of rubber significantly, thus improving the economic returns from rubber cultivation[3,4].

This paper assesses the effects of selected environmental and technological factors on rubber production in the RRIM Economic Laboratory. The environmental factors considered are rainfall, tapping days and wintering while the technological factors are improved tapping technique (controlled upward tapping) and yield stimulation.

The RRIM Economic Laboratory in Kota Tinggi, Johore Darul Takzim covers an area of approximately 133 ha. Of this area, only 103 ha are under mature rubber — 60% RRIM 600 clones and 40% RRIM 623 and RRIM 701 clones. This area of 103 ha is being used to test the Incentive Wage Concept which was formulated by the RRIM as an alternative approach to developing agricultural land in the country. Under this concept, the settlers or participants receive monthly wages based on an incentive system and, also, they share in the profit on the basis of individual productivity. Eighteen participants (husband-wife teams) tap the trees and maintain the 103 ha (approximately 5.7 ha per husband-wife team). This project has been in operation since 1976[5].

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DATA AND ANALYTICAL METHODS

The monthly rainfall, production and tapping days data used for analyses cover a twelve-year period 1976–87. Since the monthly rainfall record for August 1978 was not available, an estimated value was used to fill the missing cell when analyses were carried out. Stimulation data cover only the period 1984–7. This is because stimulation was introduced on *Panel BO–2* in 1984 and subsequently in mid-1986 on the upward cut when the controlled upward tapping (CUT) system was adopted.

Data analyses were carried out in two stages. In the first stage, the effect of diurnal (daily) and monthly variations of rainfall on output (yield) was assessed and in the second stage, the combined effects of rainfall, tapping days, wintering, stimulation and CUT on production were measured. For this measurement, the regression analysis based on the Cobb-Douglas model was used[6].

The general equation of the Cobb-Douglas model is as follows:

$$Y = KX_1\alpha_1 \cdot X_2\alpha_2 \cdot X_3\alpha_3 \ldots X_n\alpha_n \qquad \ldots 1$$

The logarithmic transformation of *Equation 1* gives the following linear model:

$$\ln Y = \ln k + \alpha_1 \ln X_1 + \alpha_2 \ln X_2 + \alpha_3 \ln X_3 + \alpha_n \ln X_n \qquad \ldots 2$$

In *Equation 2, Y* which represents output, is dependent on a number of variables such as rainfall, tapping days, wintering, *etc.* In practice, some variables like rainfall and tapping days can be quantified in specific units, whereas others like wintering, stimulation and change in tapping system cannot be measured in a similar manner. Hence, appropriate dummy variables have to be introduced in the model to represent the unquantifiable variables.

Thus, *Equation 2* has to be reformulated to take the following form:

$$\ln Y_t = \alpha + \sum_{i=1}^{5} \beta_i \ln X_i + \sum_{j=1}^{4} \delta_j D_j + \text{Error term} \qquad \ldots 3$$

where Y_t is the current month's yield

α is the intercept

X_1 is the previous month's yield

X_2 and X_3 are the current month's and previous month's rainfall

X_4 and X_5 are the current month's and previous month's tapping days

D_1 and D_2 represent wintering dummies, taking the value 1 for the third and fourth month respectively in a year and 0 for the other months

D_3 is the stimulation dummy, taking the value 1 for the months between January 1984 and June 1986 and 0 for the remaining period of study

D_4 represents CUT (with stimulation) dummy, taking the value 1 for the months July 1986 to December 1987 and 0 for the remaining period.

RESULTS AND DISCUSSION

Diurnal and Monthly Variations

The two-hourly average rainfall distribution patterns over the twelve-year period, 1976–87, at the RRIM Economic Laboratory are depicted in *Figures 1, 2* and *3*. Rainfall in the months of January and December was more evenly distributed over the 24-h period compared to that of the remaining months when the incidence of rainfall was mainly concentrated between 12 noon and 8 p.m.

During the first quarter of the year (January–March) and the last months of the remaining quarters of the year (June, September and December) 16%–24% of the total rainfall occurred between 6 a.m. and 12 noon *(Table 1)*. This is the period of day when tapping and latex collection are carried out by the participants. Thus, during these months there was a significant drop in tapping days. Added to this, in January and December 20% and 14% of the total rainfall respectively, occurred between 12 midnight and 6 a.m. Rainfall during these hours results in the panel being too wet to tap

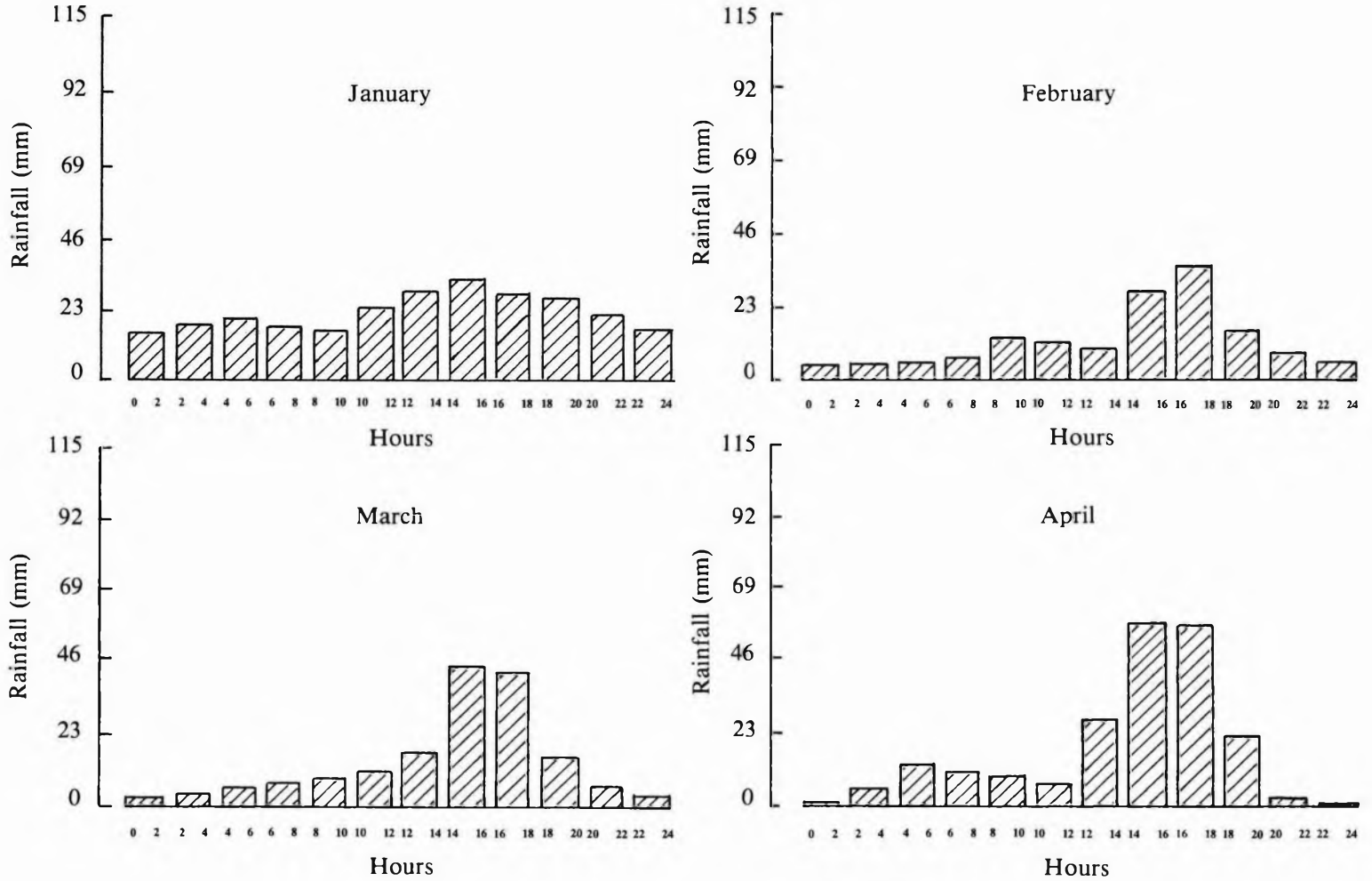

Figure 1. Diurnal variations of rainfall for January, February, March and April.

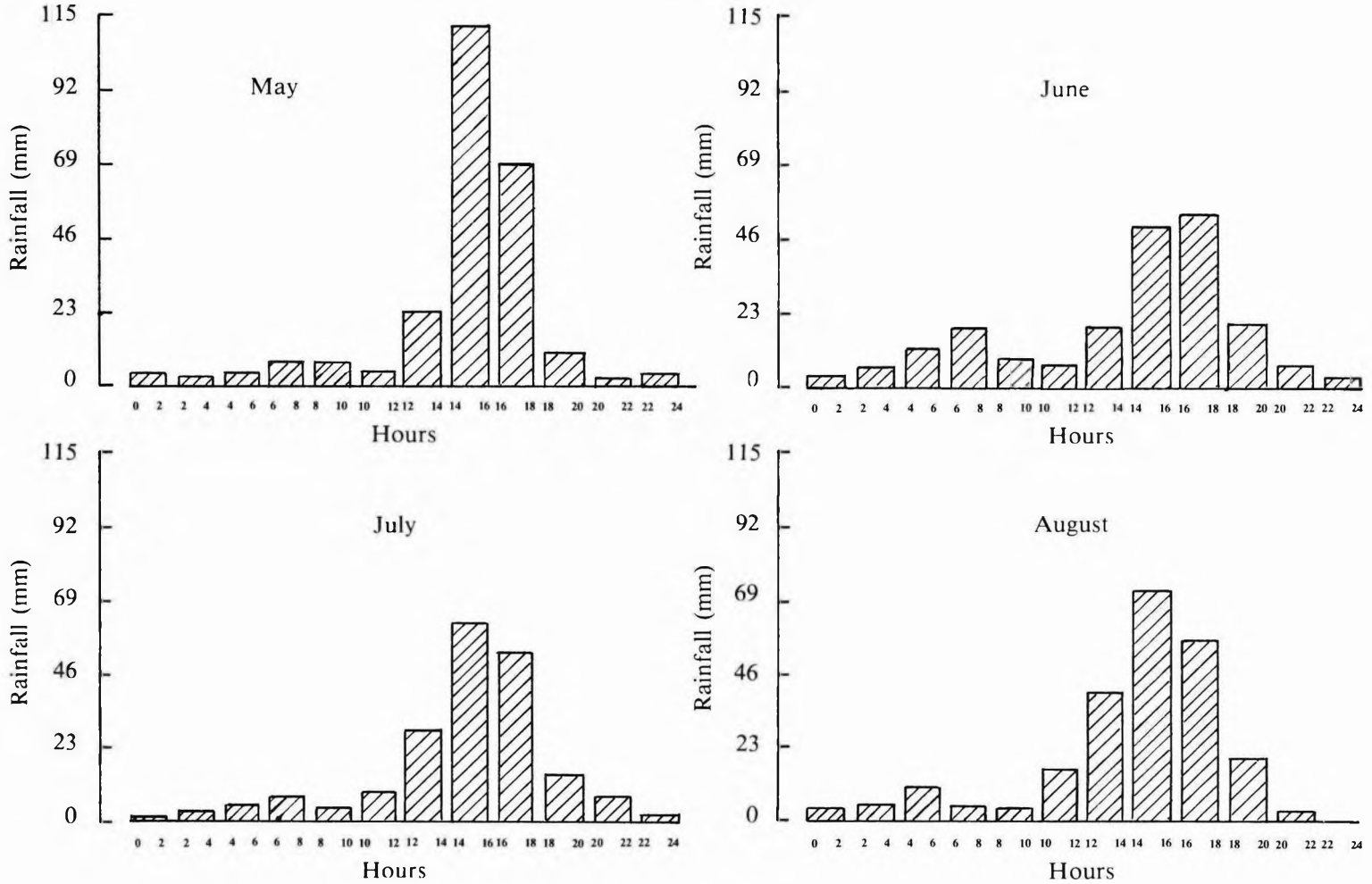

Figure 2. Diurnal variations of rainfall for May, June, July and August.

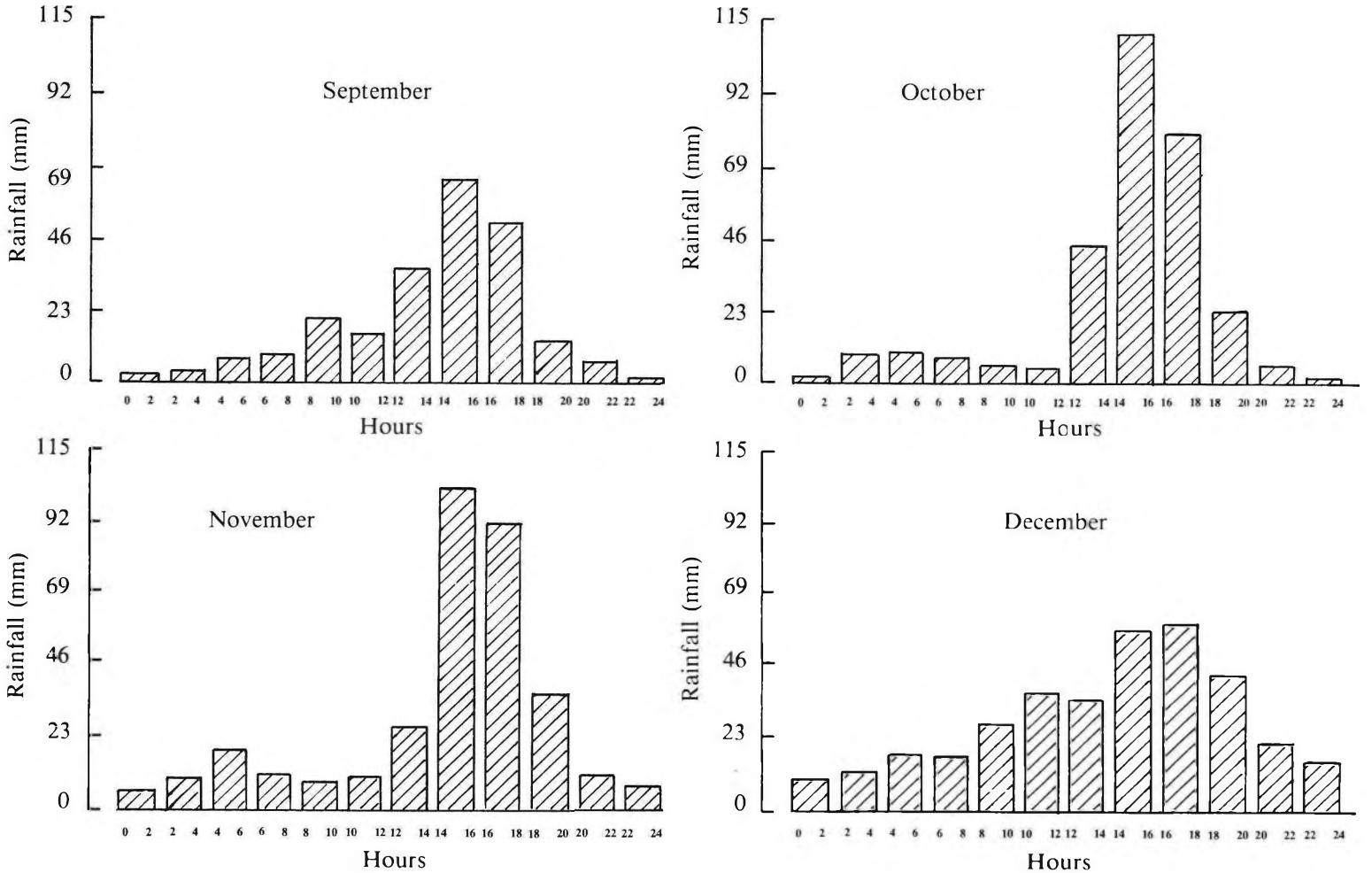

Figure 3. Diurnal variations of rainfall for September, October, November and December.

TABLE 1. AVERAGE PROPORTION OF RAINFALL OVER THE 24-H PERIOD OF THE DAY, 1976-87

Month	Average proportion of rainfall (%)			
	0-6 h	6-12 h	12-18 h	18-24 h
January	20.0	21.9	33.7	24.4
February	10.6	22.0	47.5	19.9
March	8.0	16.0	61.2	14.8
April	8.9	13.5	66.0	11.6
May	3.5	7.4	82.8	6.3
June	10.7	16.6	58.8	13.9
July	4.3	11.0	73.1	11.6
August	6.9	9.4	73.9	9.8
September	5.7	19.7	64.8	9.8
October	7.1	6.6	76.5	9.8
November	10.1	8.2	66.3	15.4
December	13.5	24.0	41.9	20.6
Annual	9.1	14.7	62.2	14.0

the following morning. Thus, causing loss of additional tapping days for these months if later tappings are not possible.

Monthly rainfall data analysis for the twelve-year period showed that the Economic Laboratory experienced heavy rain during October to January which coincides with the North-east monsoon. Of these four months, December was the wettest month with a mean rainfall of 379 mm *(Table 2)*. On the other hand, February and March were the driest months with a mean rainfall of 157-167 mm. However, year by year analyses over the twelve years showed a wide variation in the amount of rainfall during certain months; for example in January 1981, there was zero rainfall, whereas the same month in 1987 recorded the highest rainfall of 721 mm. Dale's study[7] of rainfall in Peninsular Malaysia showed that the month with the lowest rainfall had the highest coefficient of variance (C.V.) and *vice versa*. However, when the C.V. calculations were carried out this general relationship between rainfall and variability did not hold for the RRIM Economic Laboratory *(Table 2)*.

TABLE 2. DATA OF MEAN MONTHLY AND ANNUAL RAINFALL AT RRIM ECONOMIC LABORATORY, 1976-87

Month	Mean	Median	S.D.	C.V. (%)	Rain days (mean)
January	259.53	196.85	227.98	87.84	7.8
February	157.23	97.45	136.55	86.85	5.5
March	167.08	97.50	160.81	96.25	8.2
April	220.87	184.60	90.97	41.19	9.4
May	250.38	199.85	144.37	57.66	11.4
June	219.63	208.60	120.01	54.64	8.7
July	194.72	197.00	59.29	30.45	10.5
August[a]	228.63	245.30	128.07	56.02	9.1
September	254.54	247.65	75.06	29.49	12.2
October	322.23	272.35	90.85	28.19	13.3
November	334.51	296.70	154.58	46.21	14.5
December	379.37	394.35	155.55	41.00	12.3
Annual[a]	2 982.03	2 916.00	1 531.50	17.82	122.9

[a]Data for eleven years only

The mean monthly rainy days over the twelve years are also depicted in *Table 2*. A rainy day is defined as the day in which the rainfall exceeds 0.25 mm for a 24-h period. February, the driest month of the year, had the lowest mean number of rainy days (5.5 days) while November had the highest mean number of rainy days (14.5 days). September, October and December recorded a mean of twelve days or more. Since the wettest months (October to January) are also the highest yielding ones, loss in potential crop resulting from rain interference is expected to be substantial *(Table 3)*.

Regression Analysis

The regression analysis on the effects of wintering, tapping days, rainfall, CUT and stimulation on production is summarised in *Table 4*.

It is evident from *Table 4* that all the independent variables except D^3 (stimulation dummy) are significant at $P<0.05$. The variable $\ell n\ X_1$ (previous month's yield) with a coefficient of 0.3267 which is significant at $P<0.001$ indicates that the current month's production is expected to be high if the yield of the previous month is high. As expected, rainfall (variable $\ell n\ X_2$) in a month reduces tapping days and, thus depresses the yield for that month. This is supported by the coefficient of variable $\ell n\ X_2$ which is -0.0633 and significant at $P<0.01$. However, the rainfall of the previous month ($\ell n\ X_3$) has a positive effect on the production of the current month. Heavy rainfall in the previous month could have resulted in less number of tapping days; in which case, the trees would have been rested from tapping for comparatively more days. Also, the moisture content of the soil would have increased because of the heavy rainfall. These conditions would have contributed to the increase in yield for the current month. This is further supported by the variable $\ell n X_5$ (previous month's tapping days) with a coefficient of -0.2125, *i.e.*, if the tapping days of the last month is increased by a unit, the corresponding yield for this month is reduced by 0.2125 unit. On the other hand,

TABLE 3. MEAN YIELD, TAPPING DAYS AND POTENTIAL YIELD LOST AT RRIM ECONOMIC LABORATORY, 1976-87

Month	Yield (kg)		No. of normal tapping days	No. of tapping days lost due to		Output/ tapping day (kg)	Potential crop (kg) lost due to	
	Latex	Scrap		Rain	Leave and rest days		Rain (No tapping)	Leave
January	12 791	2 657	21	5	5	735.6	3 678	883
February	10 998	1 783	21	3	4	608.6	1 826	1 156
March	9 197	1 121	23	3	5	448.6	1 346	1 077
April	7 701	1 120	21	4	5	420.0	1 680	924
May	9 590	1 650	21	3	7	535.2	1 606	856
June	10 542	1 845	21	3	6	589.8	1 769	1 121
July	11 879	2 430	21	4	6	681.3	2 725	1 363
August	11 546	2 510	20	4	7	702.8	2 811	1 124
September	10 564	2 563	19	5	6	690.8	3 454	1 243
October	12 964	2 811	21	4	6	751.2	3 004	1 202
November	11 730	2 885	19	6	5	769.2	4 615	1 461
December	10 553	2 761	18	8	5	739.6	5 917	1 183
Annual	130 055	26 136	246	52	67	634.9	33 015	13 497

TABLE 4. COEFFICIENTS OF FACTORS AFFECTING THE PRODUCTION OF RUBBER

Variable	Coefficient	T-stat
α (constant)	5.5328***	7.563
$\ell n\ X_1$	0.3267***	4.845
$\ell n\ X_2$	−0.0633**	−2.792
$\ell n\ X_3$	0.05367*	2.201
$\ell n\ X_4$	0.5128***	6.669
$\ell n\ X_5$	−0.2125**	−2.598
D_1	−0.3106***	−4.924
D_2	−0.2742***	−4.347
D_3	−0.0635 P<0.1	−1.645
D_4	0.2090***	4.042

*Significant at $P<0.05$
**Significant at $P<0.01$
***Significant at $P<0.001$

R^2 : 0.6204

S.E. : 0.1830

Durbin-Watson: 2.168

Dependent variable: $\ell n\ Y$

Y = Production in kilogramme
X_1 = Previous month's yield
X_2 = Current month's rainfall
X_3 = Previous month's rainfall
X_4 = Current month's tapping days
X_5 = Previous month's tapping days
D_1 = Wintering dummy for month of March
D_2 = Wintering dummy for month of April
D_3 = Stimulation dummy
D_4 = CUT dummy

an increase in the number of tapping days in the current month (variable $\ell n\ X_4$) increases the yield of rubber for that particular month.

Wintering has a negative effect on the yield. The wintering months in the RRIM Economic Laboratory are March and April. Even though the negative effect of wintering on production for March is higher compared to that for April (coefficient of $D_1 = -0.306$ and $D_2 = -0.2742$ respectively), the total production in March (10 318 kg) is higher than in April (8821 kg). This difference in yield can be explained by the higher average tapping days in March (twenty-three days) compared to April (twenty-one days). The average number of tapping days lost due to rain in April was four days while in March it was three days *(Table 3)*. Furthermore, less rainfall in March (167 mm) compared to April (221 mm) also contributed to the higher production in March *(Table 2)*.

Stimulation with ½S d/2 tapping system was introduced in the Economic Laboratory in January 1984. This system was practised until the middle of 1986. Regression analysis showed that the application of yield stimulants had a negative effect on the production rather than a positive one (the coefficient of $D_3 = -0.0635$). This negative effect which is significant at $P<0.1$ can be attributed to the high incidence of brown bast reported in the scheme (approximately 20%), non-completion of the tasks which in turn resulted in a high number of untapped trees and improper application of yield stimulants by some of the participants. Due to the high incidence of dryness (brown bast) in the base panels, CUT with stimulation was introduced in July 1986. The coefficient of the variable D_4 (CUT dummy) of 0.2090, which is significant at $P<0.001$, indicated that CUT with stimulation had a positive effect on the yield of trees.

Further, the regression analysis showed that the selected factors namely rainfall, tapping days, wintering and stimulated tapping systems explained approximately 62% ($R^2 = 0.6204$) of the total variation in the production of rubber in the RRIM Economic Laboratory. The remaining 38% of the production variation could be due to other factors such as age of the trees, soil fertility, daily variation of temperature, *etc.*, which have not been considered in this study.

CONCLUSION

The extent to which rainfall interferes with the tapping process depends on its diurnal variation and intensity. Thus, a proper understanding of rainfall pattern in a given locality will assist the rubber grower to minimise his loss of crop due to rainfall. Heavy rain which falls during the night wets the tapping panel, which in turn

results in late tapping or non-tapping the following day depending on the intensity of panel wetness. In this situation, the grower can minimise his loss of crop by introducing rainguards on the trees[8]. Presently, these rainguards are of no help when rain occurs between 6 a.m. and 12 noon which cause partial or complete washout of the crop if tapping of the trees has commenced. Thus, there is a need for research on preventive methods that would minimise crop loss during tapping and collection time. In spite of crop loss due to rain, output can be improved if appropriate exploitation techniques and tapping systems together with the use of stimulants are adopted.

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REFERENCES

1. WYCHERLEY, P.R. (1963) Variation in the Performance of *Hevea* in Malaya. *J. trop. Geogr.*, **17,** 143.
2. HARIDAS, G. AND SUBRAMANIAM, T. (1985) A Critical Study of the Hydrological Cycle in a Mature Stand of Rubber. *J. Rubb. Res. Inst. Malaysia,* **33(2),** 70.
3. JAMES NAYAGAM, ABRAHAM, P.D. AND YONG, H.W. (1986) Economic Returns from Selected Stimulated Tapping Systems. *Proc. Int. Rubb. Conf. Kuala Lumpur,* **3,** 527.
4. VANAJA, V., YUSOF, M.S., PHANG, A.K. AND RAWIAN, M.A. (1987) Controlled Upward Tapping with Stimulation: Preliminary Results. *Plrs' Bull. Rubb. Conf. 1985 Kuala Lumpur,* **3,** 527.
5. ARIFFIN BIN MOHD. NOR AND JAMES NAYAGAM (1984) *Incentive Wage Concept: An Alternative Approach to Land Development Schemes in Malaysia.* Kuala Lumpur: Rubber Research Institute of Malaysia.
6. DILLON, J.L. (1968) *The Analysis of Response in Crop and Livestock Production.* Sydney: Pergamon Press (Aust.) Pty. Ltd.
7. DALE, W.L. (1960) The Rainfall of Malaya, Part II. *J. trop. Geogr.,* **14.**
8. CHEW, O.K., GAN, L.T., *et al.* (1986) A New Rainguard Technique (Ebor Eaves) for Improving Exploitation of Rubber. *Proc. Int. Rubb. Conf. 1985 Kuala Lumpur,* **3,** 425.

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