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Improved Ageing of Natural Rubber by Chemical Treatments

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Chemical treatments of raw natural rubber are shown to improve the Plasticity Retention Index of the finally processed material. The effects of chemical concentration and length of soaking time on different types of coagula are shown. The significance of these improvements in mastication and mixing in high temperature internal mixers is demonstrated. Increased resistance of vulcanisates of PRI-improved rubbers to oven-ageing is obtained with the exception that those treated with oxalic acid show impaired ageing in non-black compounds. High temperature dynamic testing of vulcanisates of treated rubbers is discussed.

Natural rubber present in the latex vessels of the tree has a high molecular weight and is well protected by anti-oxidants but, between tapping and baling, certain collection and processing practices and some environmental conditions can impair these desirable characteristics.

The Plasticity Retention Index (PRI) test (BAKER *et al.*, 1966) has been in use for three years in Malaysia to monitor the loss of these characteristics and has proved itself to be of considerable value. The test gives a measure of the oxidisability of rubber which may be affected by the concentration of anti-oxidants and metal-chelating agents and by any partial oxidation it may have already suffered. Because these different causative features exist some confusion has arisen as to the interpretation of the test.

Reduction in PRI

The factors which lower the PRI of various forms of NR are fairly well documented (BATEMAN AND SEKHAR, 1966; SIVABALASUNDERAM AND NADARAJAH, 1966; NADARAJAH *et al.*, 1967; O'CONNELL, 1966) and are listed below:

(1) exposure to direct sunlight, especially if the rubber is dry;
(2) adventitious contamination with copper, iron or manganese;
(3) excessive soaking in water;
(4) excessive crepeing particularly with fine nip settings;
(5) over-heating during drying or incorrect drying procedures; and
(6) centrifugation, which causes accumulation of trace metals in the skim fraction.

The importance of these factors varies widely and may or may not be significant, depending upon other parameters *e.g.*, time, concentration of added chemical, etc.

Recent observations (GURUSAMY, 1967; GRAHAM, 1967) have revealed that the PRI values of rubbers processed from acid-coagulated or auto-coagulated field latex fall as the length of time between coagulation and milling is increased. Also, if very small quantities of unchelated (active) copper are present this fall in PRI is accentuated and can be serious within a short time with auto-coagulated rubbers. These effects are illustrated in *Figure 1.*

It was noted also that the amount of copper retained in the rubbers increased with the time the coagulum was kept both in the presence and absence of added copper. In the contaminated samples the copper contents ranged from 3 to 5 parts per million, levels hitherto considered unimportant.

Increase in PRI

The PRI values of rubbers have been shown to be increased by soaking the coagulum,

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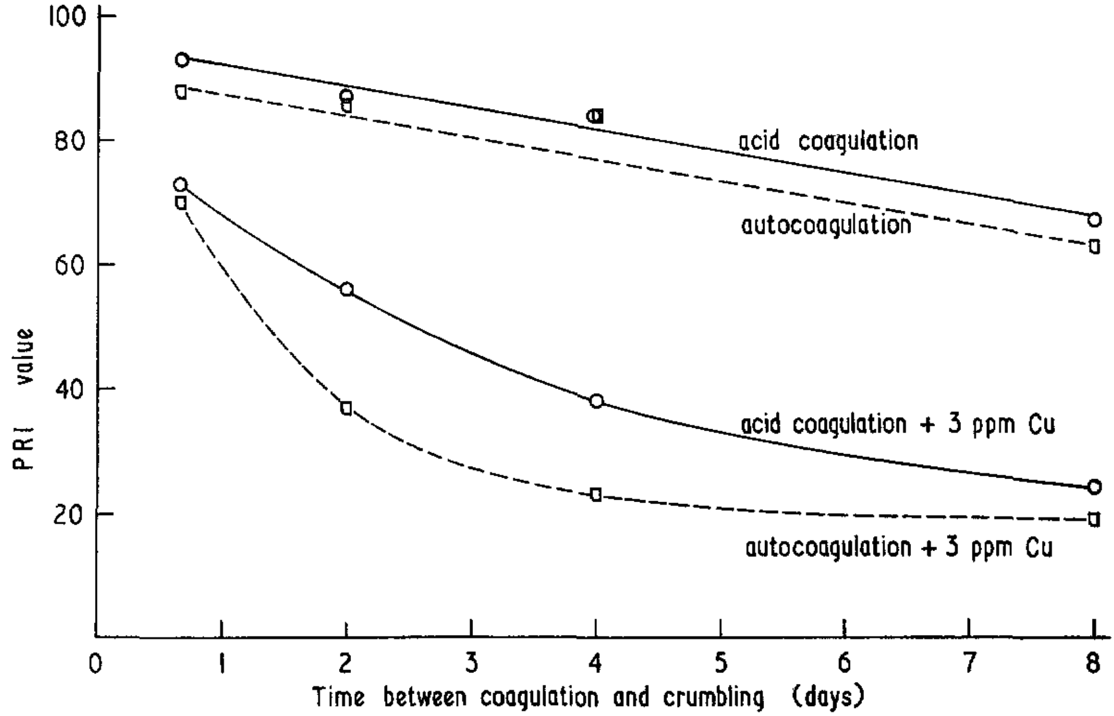


Figure 1. Changes in PRI of latex Heveacrumb due to delayed processing and contamination by copper ions.

usually in a comminuted or crumbled form, in aqueous solutions of oxalic acid, phosphoric acid (SEKHAR, 1965; SMITH AND SEKHAR, 1966) sodium oxalate, the disodium salt of ethylenediaminetetraacetic acid (EDTA) and pyrogallol (SIVABALASUNDERAM AND NADARAJAH, 1966).

FURTHER EXPERIMENTS ON SOAKING TREATMENTS

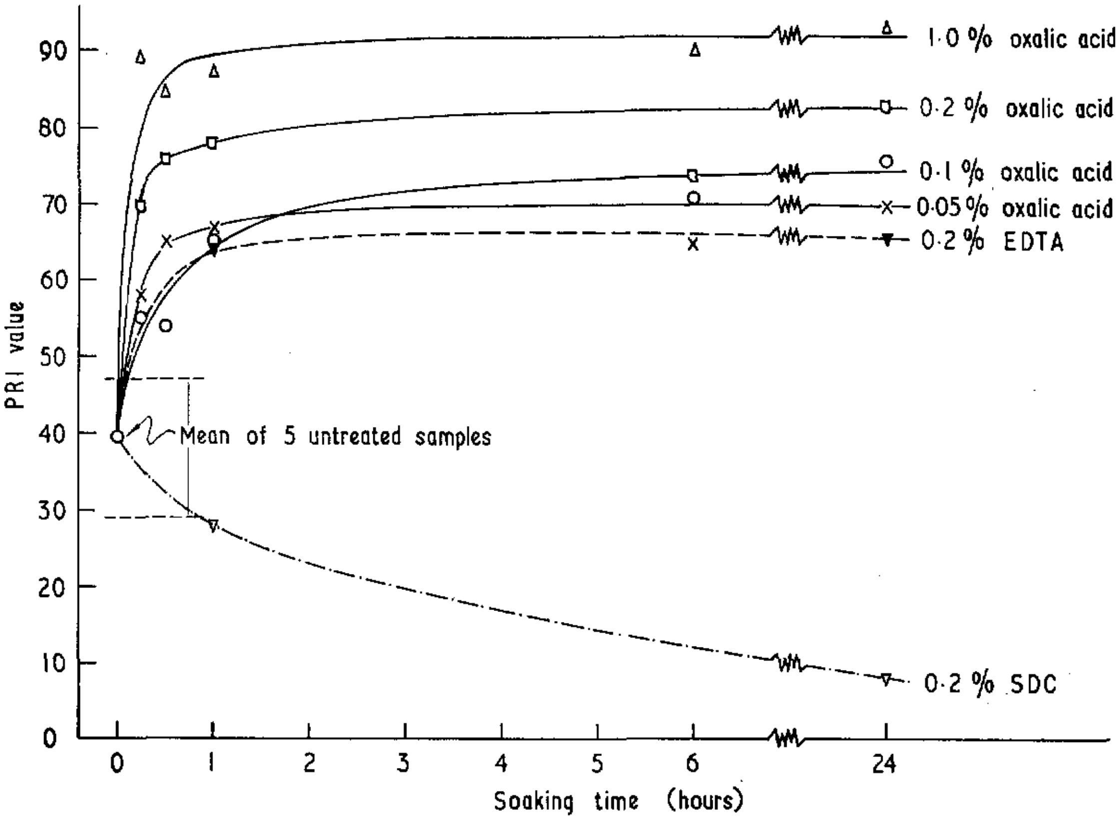
Granulated estate cuplump material was allowed to soak in water for eight days and was then crumbled. The crumbs were divided and treated with aqueous solutions of different reagents for various times before drying at 105°C.

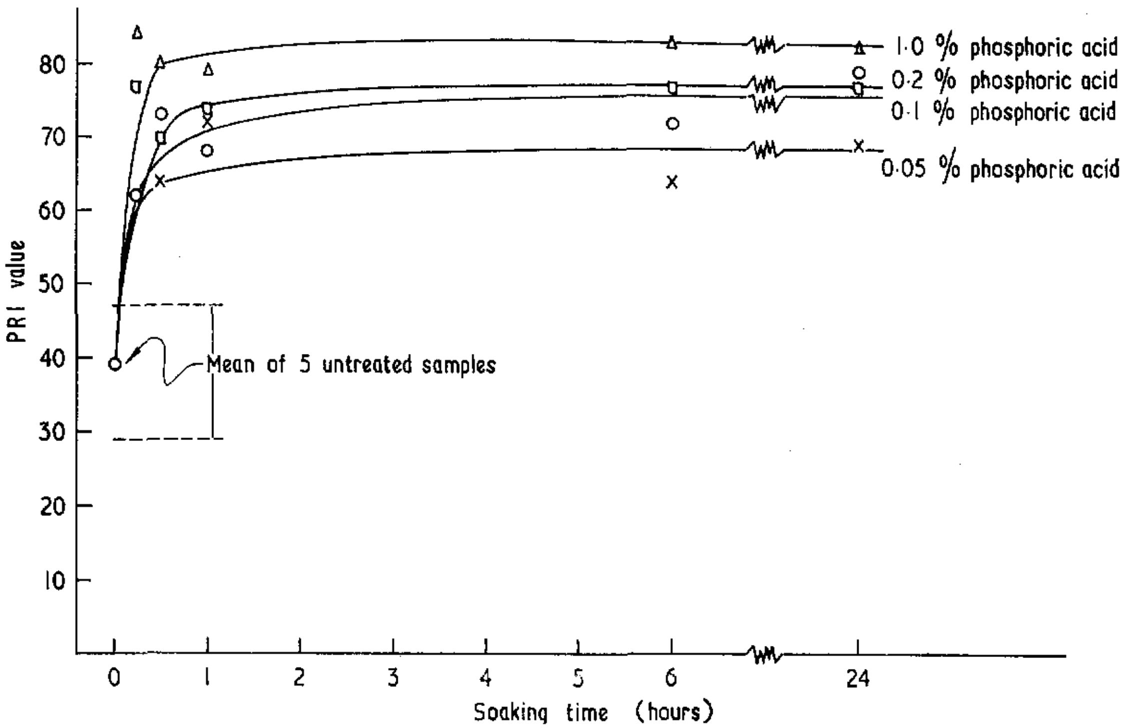
Figures 2 and *3* show the effects on PRI of the various treatments, which were beneficial except in the case of sodium diethyldithiocarbamate (SDC) treatment. Oxalic and phosphoric acids were the most effective and for this type of raw material little appeared to be gained in prolonging the soaking beyond 1 or 2 hours at 0.2 weight per cent concentration.

Remillers' field coagulum consisting of 75% cuplumps and 25% tree lace was similarly treated with 1.0% oxalic acid and 1.0% phosphoric acid for times up to 24 hours. Results presented in *Table 1* show that soaking in either acid solution for 1 hour suffices to give a substantial rise in PRI.

The copper and manganese contents were approximately 5 and 7 p.p.m., respectively, and did not alter with the treatments. Further experiments showed that 0.5% of either acid was equally effective if soft water were used instead of artesian water having a high calcium content.

Samples of remillers' scrap of varying visual qualities were used for a series of separate daily acid-soaking experiments in which each day represented a different starting material. *Figure 4* illustrates the effect on the crumbs produced from these materials by soaking in 0.5% oxalic





Figures 2 & 3. Changes in PRI of estate cuplump material effected by various soaking treatments.

TABLE 1. EFFECT ON PRI OF SOAKING REMILLERS' FIELD COAGULUM CRUMB IN OXALIC AND PHOSPHORIC ACID SOLUTIONS

Acid solution	Soaking time (h)	Unaged Wallace plasticity	PRI	Mean PRI
None	-	44	39	39
1% Oxalic	1	42.5	79	
	2	44	74	
	4	44	75	76
	8	45	76	
	24	45	76	
1% Phosphoric	1	43.5	74	
	2	44.5	72	
	4	44.5	72	73
	8	44.5	70	
	24	44	75	

acid and in 0.5% phosphoric acid for 2 hours before drying.

It is clear that not only is the PRI consistently raised by the treatments but that there is a striking improvement in the uniformity of the rubber, the benefits of which are discussed later.

The effects of soaking treatments on copper-contaminated field latex coagulum have so far been disappointing *(Table 2)*. Oxalic acid has shown the greater effect in raising PRI values but the PRI levels of the processed rubbers after treatment are still low compared with those made from uncontaminated and unmatured coagulum.

The PRI values of skim rubbers are usually lower than rubbers from field latex and can often be very low. Improvement in the PRI of skim rubbers by oxalic acid treatment has already been demonstrated (SEKHAR, 1965; BATEMAN AND SEKHAR, 1966). Phosphoric

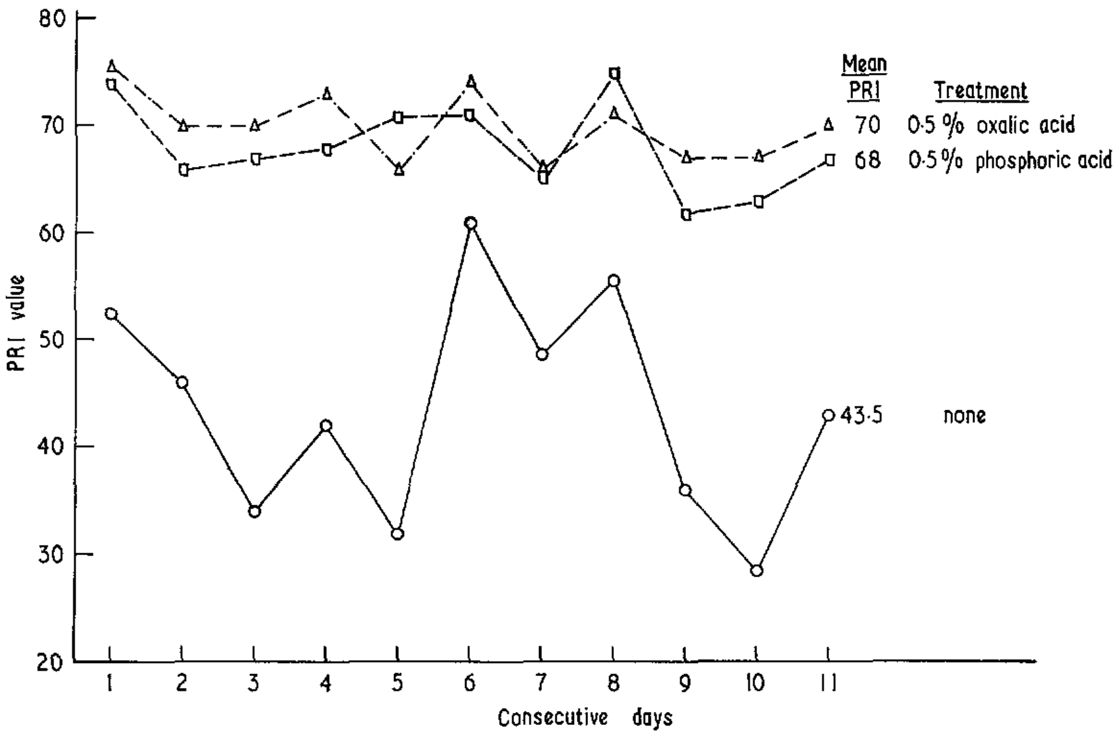


Figure 4. Effect on PRI of soaking remillers' cuplump and tree lace crumb in acid solutions.

TABLE 2. EFFECT OF ACID SOAKING ON CRUMB FROM FIELD LATEX COAGULUM CONTAMINATED WITH COPPER AND MATURED

Latex	Type of coagulation	Maturation (days)	Cu addition (p.p.m.)	Acid soaking treatment*	PRI
A	Acid	1	–	–	91
	,,	1	2	–	86
	,,	1	2	oxalic	95
	,,	1	10	–	27
	,,	1	10	oxalic	60
	Auto	3	–	–	61
	,,	3	2	–	26
	,,	3	2	oxalic	56
	,,	3	10	–	oxidised
	,,	3	10	oxalic	oxidised
B	Acid	1	–	–	91
	,,	4	–	–	85
	,,	4	–	phosphoric	84
	,,	1	3	–	79
	,,	4	3	–	70
	,,	4	3	phosphoric	70
	Auto	1	–	–	87
	,,	4	–	–	57
	,,	4	–	phosphoric	65
	,,	1	3	–	73
	,,	4	3	–	25
	,,	4	3	phosphoric	31

*0.2% Aqueous solution for 4 hours

acid treatment has now also been shown to raise the PRI of skim but the magnitude of the increase is less. Crumbs from two acid coagulated skim latices were divided and part-treated with sodium hydroxide to reduce the protein content. These portions were sub-divided and treated with either 0.2% oxalic acid or with 0.2% phosphoric acid for 4 hours. The properties of the raw rubbers after high temperature drying are given in *Table 3*. Oxalic acid gave a high PRI in each case but phosphoric acid gave only a small PRI increase with the high copper latex (A) and a moderate increase with the low copper latex (B). A small reduction in copper content was achieved with both oxalic and phosphoric acids.

Treatment of tree lace with either oxalic or phosphoric acid usually produces only a small increase in the PRI value. Tree lace is more susceptible to sunlight degradation than other forms of raw rubber since it dries quickly, has a large surface area and is generally more exposed on the tree.

The results of an experiment in which tree lace was treated with 0.2% oxalic acid before and after 10 hours' sunlight ageing are given in *Table 4*.

The trivial improvement in PRI of the unexposed tree lace suggests that the material may

TABLE 3. ACID TREATMENTS OF SKIM LATEX COAGULA WITH AND WITHOUT PRIOR PROTEIN REDUCTION BY SODIUM HYDROXIDE

Skim latex	NaOH treatment	Acid treatment	Nitrogen (%)	Copper (p.p.m.)	Raw Mooney viscosity (V_R) MS 1+4′, 100°C	PRI
A	–	None	1.9	5.6	53	26
	–	Oxalic	2.1	4.9	53	90
	–	Phosphoric	2.0	4.8	53	36
	Yes	None	1.4	3.4	33	30
	Yes	Oxalic	1.4	3.0	51	94
	Yes	Phosphoric	1.4	2.7	52	44
B	–	None	3.0	1.9	61	68
	–	Oxalic	3.0	1.5	61	94
	–	Phosphoric	2.9	1.5	60.5	85
	Yes	None	1.4	<1	51	21
	Yes	Oxalic	1.3	<1	52	96
	Yes	Phosphoric	1.3	<1	48	65

TABLE 4. EFFECT OF SOAKING TREE LACE IN 0.2% OXALIC ACID BEFORE AND AFTER SUNLIGHT-AGEING

Sample	Treatment	Wallace P_o	PRI
Tree lace	None	42	46
	Oxalic acid	44	50
Sunlight-exposed tree lace	None	30.5	41
	Oxalic acid	33	39

have already been sunlight-degraded while the effect of further sunlight exposure was to reduce the viscosity rather than cause a drastic lowering in PRI. Oxalic acid treatment of this material did not raise the PRI.

MASTICATION AND MIXING OF RUBBERS OF DIFFERENT PRI

In any rubber-producing factory it is difficult to achieve complete uniformity of the PRI values because of the many factors which can affect it, not the least of which are the different sources of material and the often unavoidably different time delays between harvesting and processing. Chemical treatment provides an opportunity of producing a more uniform material which the manufacturers of rubber products will find to be of considerable benefit.

The manufacturer who employs internal mixers for mastication and mixing rubber has to ensure that each batch of mixed compound is within a fairly narrow range of viscosity so that shaping processes such as calendering, extrusion and injection moulding can be performed without difficulty. Also, if the viscosity of the mix is too low, important physical properties of the final manufactured article can be impaired (BATEMAN AND SEKHAR, 1966; BAKER AND GREENSMITH, 1966).

On mill mastication at 150°C the chemically treated rubbers follow the expected exponential decay of viscosity which was established for market grades of natural rubber (GREENSMITH, 1966) and thus the PRI values will give a useful indication of the degree of breakdown during mastication and mixing in high temperature internal mixers. It is probably in this respect that knowledge of the PRI values of rubbers is of the greatest benefit to the rubber user.

Rubbers of differing PRI and having the same initial Mooney viscosities were masticated in a laboratory Banbury mixer (00C type) using a full capacity charge of 2400 ml, a starting temperature of 100°C (rotor and jacket) and 80 rev/min rotor speed. The results are shown in *Figure 5*, the dump temperatures being those recorded on the Banbury chart.

If a fixed mastication time is used, say 4 minutes, then it is clear that a wide range of viscosities will result from the different PRI rubbers (see *Figure 6*, drawn from the curves of *Figure 5*.)

Somewhat surprisingly the dump temperatures after a fixed mastication period vary very little and the procedure of dumping at a fixed temperature will not give a much narrower range of viscosities from the different PRI rubbers. Between the highest and lowest PRI rubbers the difference in total power consumption for a given cycle was between 5 and 10% and the peak power loads differed by 12%.

A similar study was carried out on Banbury mixing using a standard base compound:

Rubber	100	parts
Dutrex R	5	,,
Zinc oxide	4	,,
Stearic acid	1.5	,,
Nonox HFN	1.5	,,

and three fillers. The standard conditions used for the mixing were:

Charge	2000 ml
Rotor speed	80 rev/min
Starting temperature	100°C

Mixing cycle:

0 min	—	add rubber
0.5 "	—	add other ingredients
2 "	—	sweep
3 "	—	dump

The results presented in *Figure 7* show that the viscosities of the mixed batches are considerably dependent on the PRI values of the rubbers used and that an unacceptably wide range of batch viscosities are obtained if the rubbers used are not sufficiently uniform in PRI. The

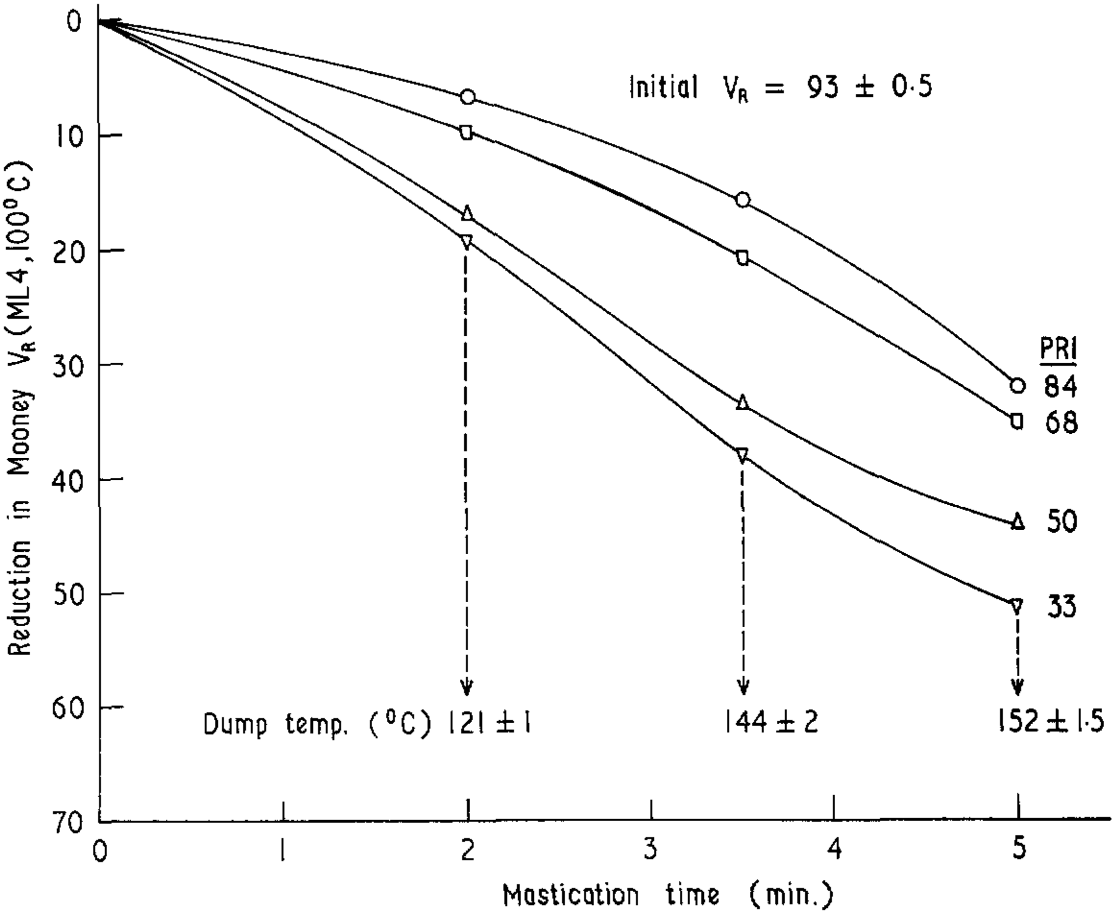


Figure 5. *Banbury pre-mastication behaviour of rubbers having different PRI values.*

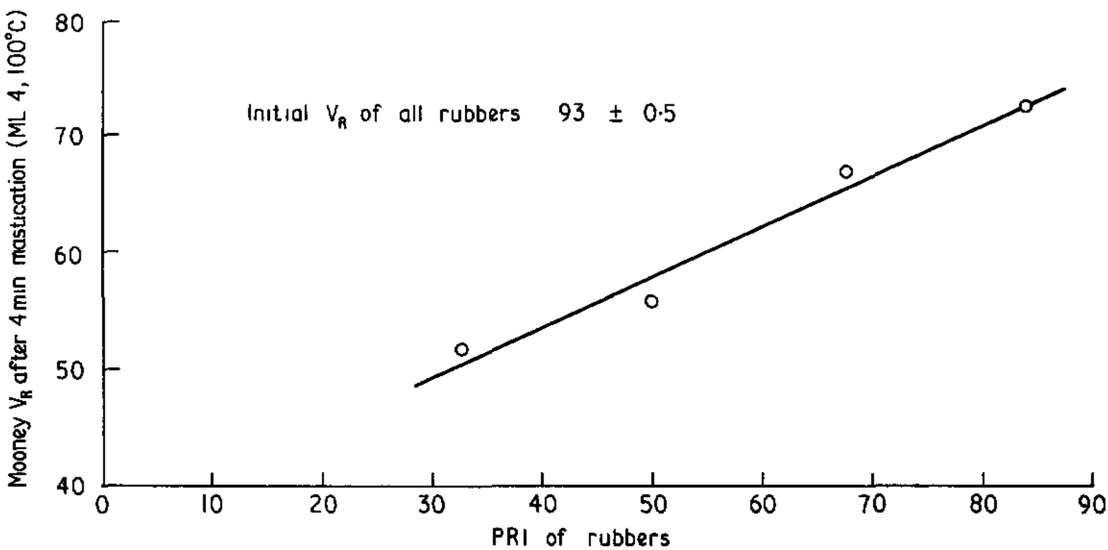


Figure 6. *Dependence of the extent of mastication on the PRI values of the rubbers used.*

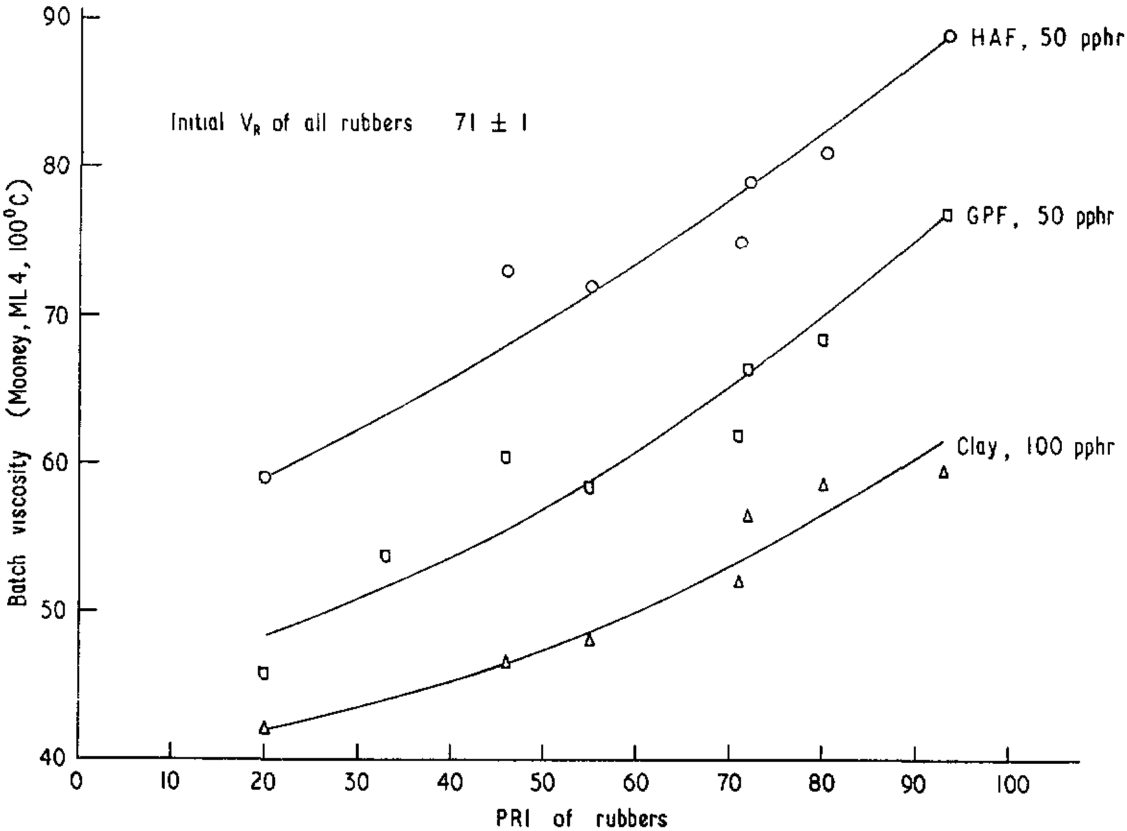


Figure 7. Variation of mix viscosity on the PRI values of the rubbers used.

differences in power consumption during the cycles, between the lowest and highest PRI rubbers, were from 6 to 9% for the various fillers. There were no significant differences between peak loads for a given filler.

AGEING PROPERTIES OF CHEMICALLY TREATED RUBBERS

The better resistance to oven-ageing of unprotected and protected gum vulcanisates of natural rubbers having high PRI values relative to those of lower PRI values has been clearly shown for market grades having 'naturally' different PRI values (GREENSMITH, 1966).

The oven-ageing properties of unprotected gum sulphur/CBS vulcanisates prepared from the remillers' rubbers described in *Table 1* were examined *(Figure 8)*.

The surprising result obtained was that the oxalic acid treated rubbers all showed poorer ageing than the control although the PRI values were high. However, the phosphoric acid treated rubbers showed improved ageing properties consistent with their increased PRI values. Stress relaxation measurements in air at 100°C *(Figure 9)* confirmed the results of the oven-ageing.

In the same gum compound protected with 2 parts per hundred of rubber (p.p.h.r.) of N-(1,3-dimethylbutyl) N′-phenyl-p-phenylenediamine (Santoflex 13), the poorer retention of tensile properties of the oxalic acid treated rubbers was still detectable and was again confirmed by stress-relaxation studies *(Figure 10)*. With this type of anti-degradant, the difference in ageing properties is trivial but with smaller

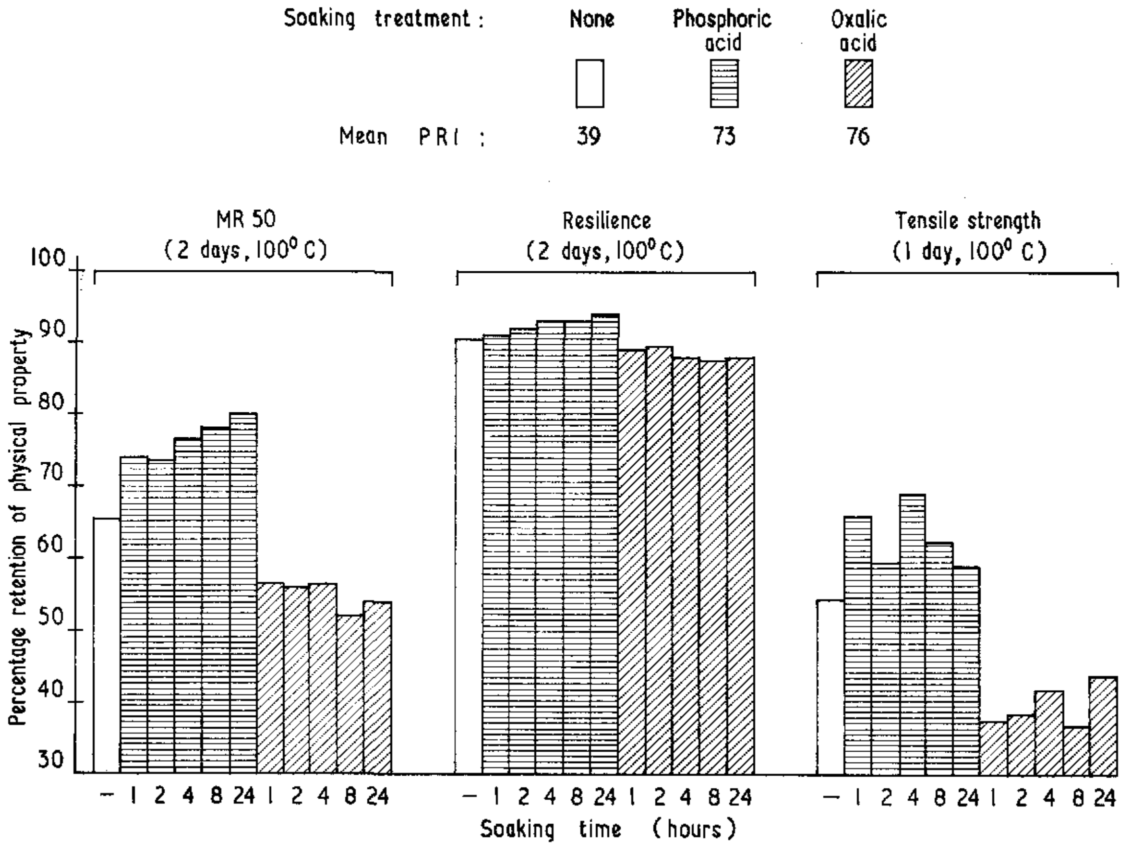


Figure 8. Oven-ageing properties of rubbers treated with phosphoric and oxalic acids; unprotected gum vulcanisates.

quantities of less effective anti-oxidants the differences are likely to be significant.

The oven-ageing properties of vulcanisates made from latex rubbers having naturally high PRI values are also adversely affected if the coagula are soaked in oxalic acid during processing. This poorer ageing is evident even though the PRI values are marginally increased by the soaking treatment *(Table 5)*.

Indications of the deleterious effects of oxalic acid soaking were independently observed (SMITH, 1967) and the conclusion was drawn by this author that PRI gave little indication of vulcanisate ageing performance. In the light of the evidence given in this paper the present author cannot agree with this conclusion although there is now this specific exception of oxalic acid treated rubbers to the general correlation of PRI and vulcanisate ageing properties.

Oxalic acid very effectively chelates traces of certain metallic ions, particularly copper, which play a dominant catalytic role in high temperature (about 140°C) oxidation of natural rubber such as occurs in high temperature mastication and the PRI test itself. It is suggested that oxalic acid also has the unfortunate effect of either leaching out natural amine anti-oxidants or converting them to inactive substituted ammonium salts. The natural amine anti-oxidants play an important role in rubber ageing at more moderate temperatures

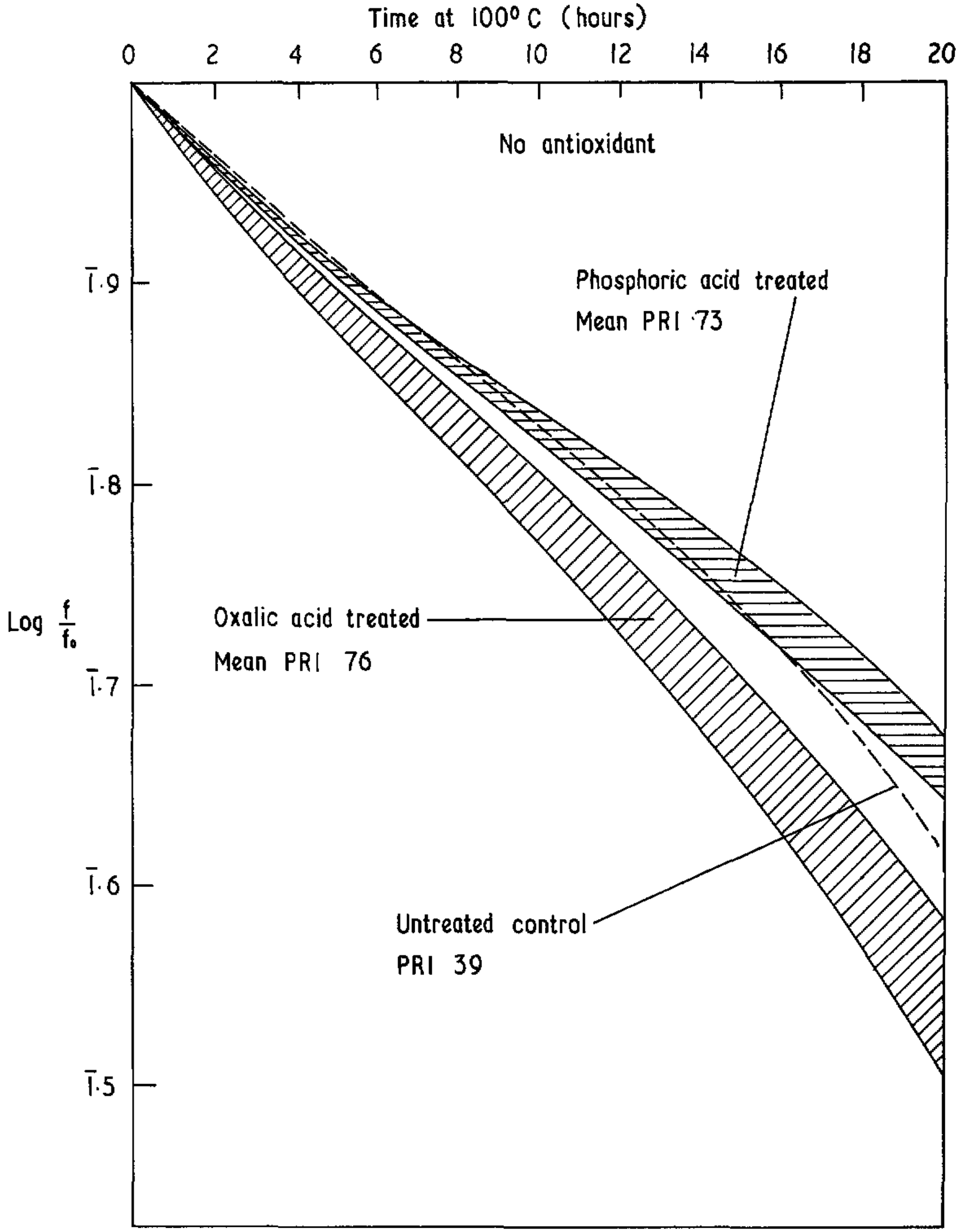


Figure 9. Stress relaxation behaviour of rubbers treated with phosphoric and oxalic acids; unprotected gum vulcanisates. The shaded areas enclose the stress relaxation curves of the five rubbers soaked for varying times in each reagent.

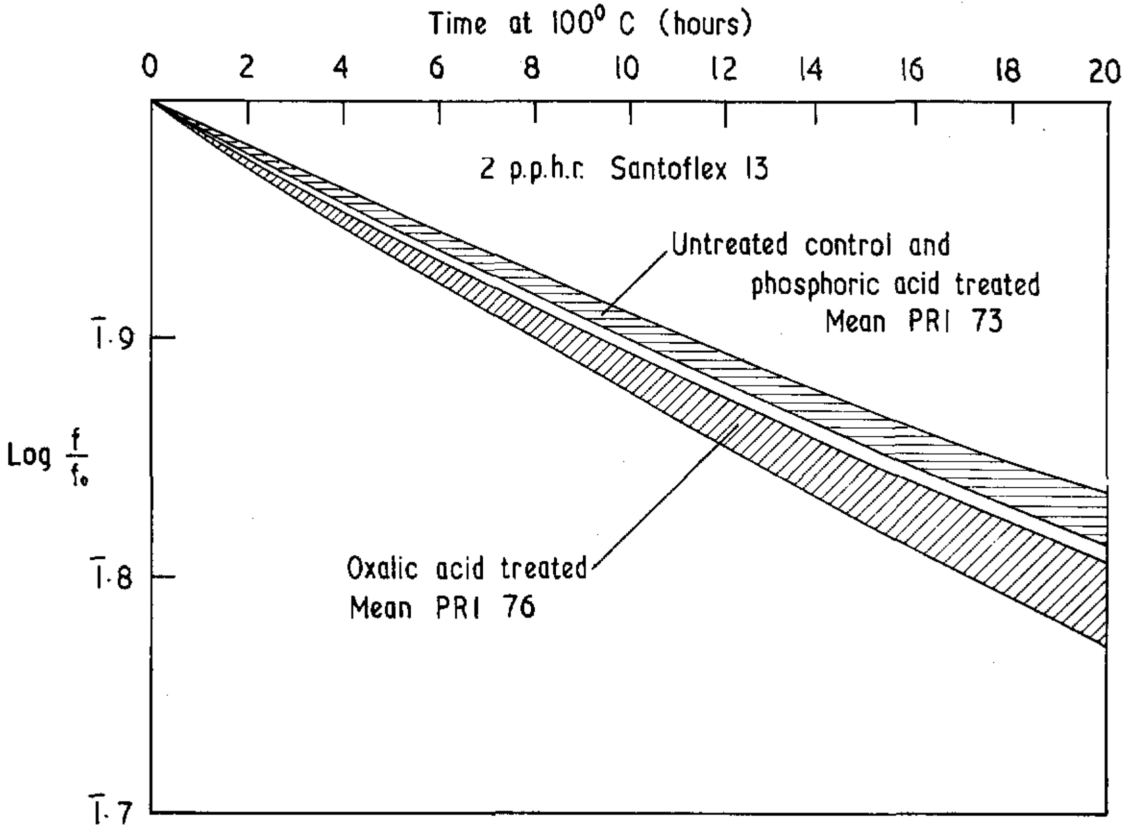


Figure 10. Stress relaxation behaviour of rubbers treated with phosphoric and oxalic acids; well protected gum vulcanisates. The shaded areas enclose the curves for the five soaking times in each reagent.

TABLE 5. EFFECT OF OXALIC ACID SOAKING ON THE OVEN-AGEING PROPERTIES OF HEVEACRUMB (FROM FIELD LATEX) IN UNPROTECTED GUM VULCANISATES

Coagulation method	Soaking treatment	PRI	MR 100† (kg/cm²)		Resilience (%)		Tensile strength (kg/cm²)	
			Initial	Aged, 2 days at 100°C	Initial	Aged, 2 days at 100°C	Initial	Aged, 2 days at 100°C
Acid	None	91	5.6	4.1	90.1	83.2	276	131
Acid	Oxalic acid*	99	5.4	2.8	89.7	78.0	267	54
Auto-coagulation (3 days)	None	61	5.9	4.2	89.9	82.6	282	94
Auto-coagulation (3 days)	Oxalic acid*	77	5.4	3.0	89.7	78.2	277	30

*0.2% Solution for 4 hours †Relaxed modulus at 100% extension

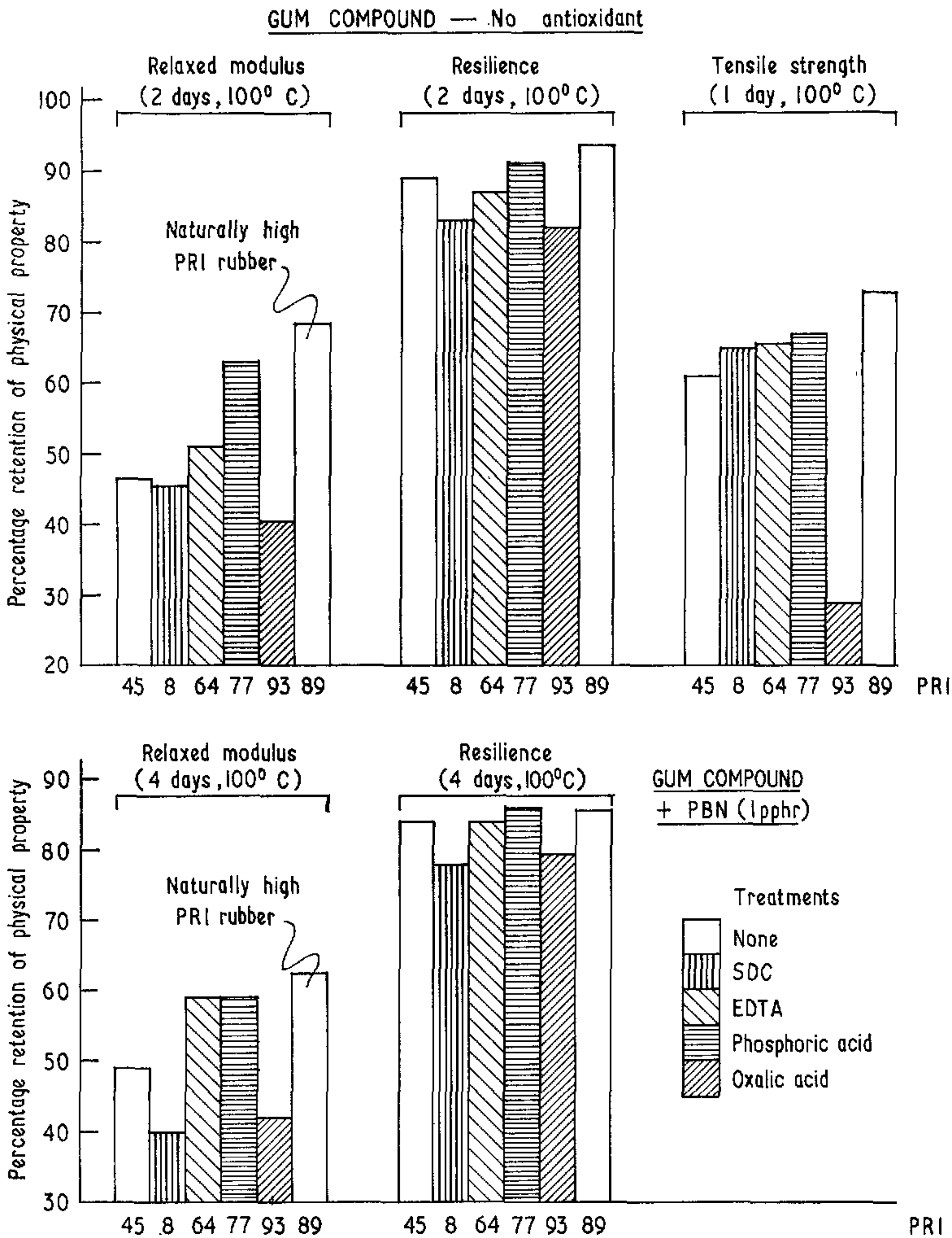


Figure 11. Oven-ageing properties of gum vulcanisates prepared from chemically treated cuplump Heveacrumb and a naturally high PRI latex Heveacrumb sample (PRI 89).

(below about 110°C) at which they are more thermally stable and clearly should not be lost.

The oven-ageing properties of the estate cup-lump rubbers treated with various reagents (described earlier in this paper; *Figures 2* and *3*) and a naturally high PRI rubber were examined in an unprotected gum compound, a protected gum compound and a protected HMF black-loaded carcass compound. A conventional sulphur/CBS curing system was used throughout, compound viscosities were kept within a narrow range and vulcanisates were cured to optimum resilience and tensile strength. The initial properties of all the vulcanisates in their respective compounds were virtually indistinguishable from each other.

Typical results of the retention of properties on oven-ageing are given in *Figures 11* and *12*. In the unprotected gum compound there is a good correlation between PRI and resistance to ageing with the notable exception of the rubber treated with oxalic acid. Also the SDC treated rubber perhaps performs rather better than would be expected from its very low PRI. In the anti-oxidant protected gum compound, the oxalic acid treated rubber again shows impaired instead of improved ageing. A detailed study of this series of rubbers showed that at all concentrations and soaking times the phosphoric acid treated rubbers had improved

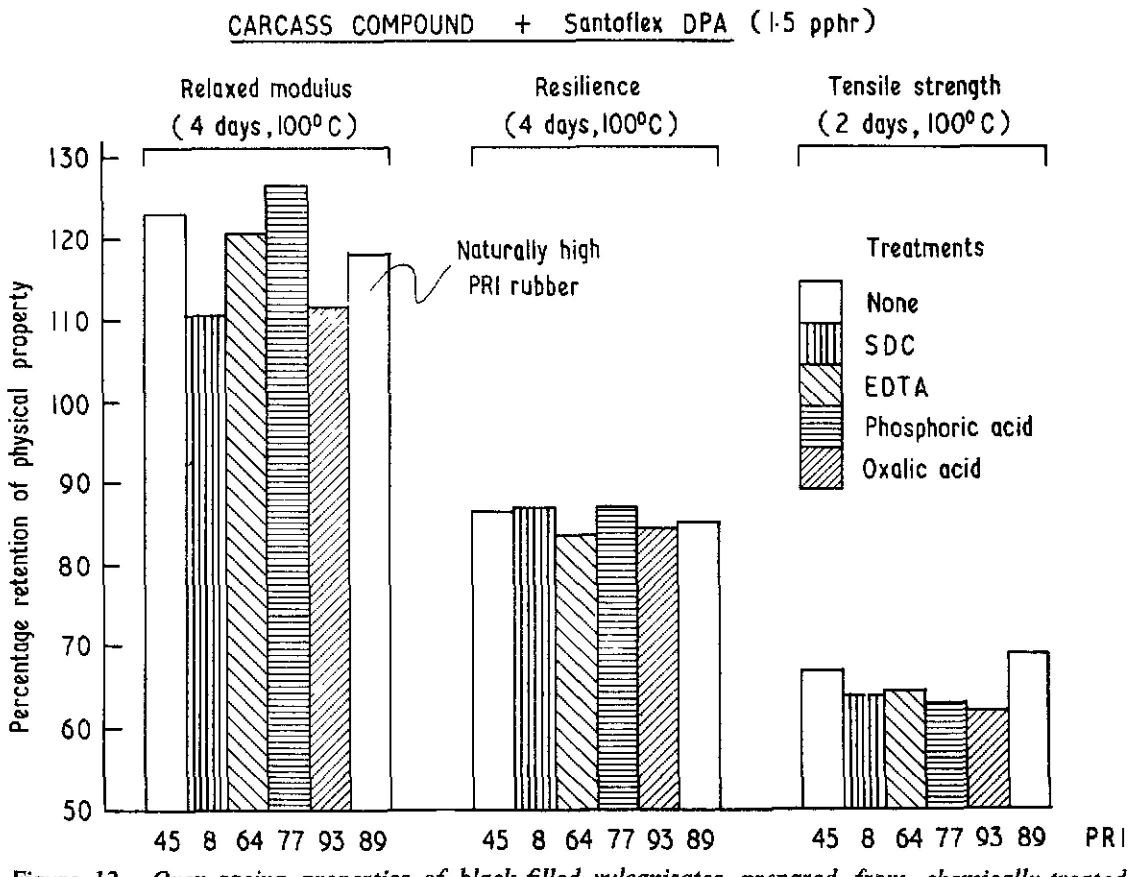


Figure 12. Oven-ageing properties of black-filled vulcanisates prepared from chemically treated cuplump Heveacrumb and a naturally high PRI latex Heveacrumb sample (PRI 89).

ageing properties, the extent of the improvement being directly related to the PRI increase. The oxalic acid treated rubbers had equivalent ageing properties to the untreated (PRI 45) control at low concentrations and short soaking times and became progressively poorer in ageing properties as soaking time and concentration were increased, despite the fact that all the PRI values were high.

In the carcass compound there are some differences in modulus behaviour but the vulcanisates are equivalent in tensile strength and resilience retention.

High temperature dynamic performance of some of this series of rubbers in the above carcass compound has been examined using the Dunlop punch fatigue test and the Goodrich flexometer. The results of these tests on the rubbers compounded to the same formulation in different laboratories are given in *Table 6.* With the exception of the rubbers soaked for 24 hours in oxalic acid solution there appears to be a trend towards improved performance with chemical treatment. The modulus and resilience of the vulcanisates were closely similar and were prepared from mixes of similar viscosities.

In the comparatively short duration of the Goodrich test and in consideration of the thickness of the test-piece, it is difficult to see how the oxidation resistance of the rubber will affect the heat build-up and it seems more likely that the acid-treated rubbers may have slightly more thermally stable network structures after cure, although the initial cross-link densities are virtually the same as the control. In an attempt to test this idea the changes in relaxed modulus and resilience of carcass compound vulcanisates of the above series of rubbers were measured after heating at 100°C and at 140°C in a closed mould; *i.e.*, under substantially anaerobic conditions.

On heating at 100°C, modulus increased while resilience fell only slightly and the differences between the rubbers do not appear significant. In contrast, at 140°C, modulus and resilience both fell appreciably and the oxalic and phosphoric acid treated rubbers showed a smaller drop than the control, indicative of a slightly more thermally stable network. It can be argued that, as the temperatures inside the shoulder of tyres seldom exceed 100°C, the changes occurring at about 140°C are of less relevance.

TABLE 6. TEST DATA RELATING TO THE HIGH TEMPERATURE DYNAMIC PERFORMANCE OF CARCASS VULCANISATES PREPARED FROM HEVEACRUMB CUPLUMP RUBBERS SUBJECTED TO VARIOUS SOAKING TREATMENTS DURING PRODUCTION

Soaking treatment and time of treatment	PRI	Dunlop punch test		Goodrich flexometer †		
		Performance rating*	Running temp. (°C)	Anvil temp. after 60 min (°C)	Dunlop resilience at 20°C (%)	Compound viscosity ML1+4′, 100°C
None	45	5.37	152	122	82.0	39
0.2 % Oxalic acid, 0.5 h	76	5.43	147	–	–	–
” ” ” 1 h	78	5.53	135	122	81.6	45
” ” ” 6 h	74	5.29	151	–	–	–
” ” ” 24 h	83	5.31	149	117	81.6	45
1.0% ” ” 24 h	93	5.14	150	114	82.0	44
0.2% Phosphoric acid, 0.5 h	70	5.42	145	–	–	–
” ” ” 1 h	74	5.47	145	121	81.1	44
” ” ” 6 h	77	5.36	143	–	–	–
” ” ” 24 h	77	5.39	142	117	81.1	47
1.0% ” ” 24 h	82	5.61	143	114	81.4	45
0.2% EDTA 1 h	64	5.39	143	124	81.4	44

* Logarithm of number of blows to failure

† Constant load (48 lb), stroke 0.2 inch, 1800 rev/min

TABLE 7. RELAXED MODULUS AND RESILIENCE CHANGES OBSERVED ON CLOSED MOULD HEATING OF CARCASS COMPOUND VULCANISATES* PREPARED FROM CUPLUMP RUBBERS SUBJECTED TO VARIOUS SOAKING TREATMENTS

Soaking treatment and time of treatment	Initial MR 100† (kg/cm²)	Initial resilience (%)	Heated 136 h at 100°C		Heated 8 h at 140°C	
			△ MR 100 (kg/cm²)	△ Resilience (%)	△ MR 100 (kg/cm²)	△ Resilience (%)
None	15.2	80.6	+4.0	−1.5	−3.6	−8.2
0.2% Oxalic acid, 1 h	15.1	80.9	+4.9	−1.0	−2.8	−7.0
,, ,, ,, 24 h	15.5	80.6	+3.7	−0.9	−2.9	−6.8
1.0% ,, ,, 1 h	15.1	81.0	+3.8	−0.4	−2.6	−6.9
,, ,, ,, 24 h	15.1	80.9	+3.7	−0.2	−2.7	−6.4
0.2% Phosphoric acid, 1 h	15.1	81.1	+4.5	−0.5	−3.0	−8.6
,, ,, ,, 24 h	14.9	80.8	+3.9	−1.5	−3.0	−7.7
1.0% ,, ,, 1 h	14.9	80.3	+3.9	−0.9	−3.0	−7.1
,, ,, ,, 24 h	14.9	81.0	+4.5	−1.6	−2.6	−7.0
0.2% EDTA 1 h	15.0	80.5	+3.6	−1.9	−3.3	−8.2

* Initially cured 35 min at 140°C　　† Relaxed modulus at 100% extension

It is concluded that the benefits in using acid-treated rubbers in tyre carcass compound is marginal with the important exception that use of the high PRI rubbers will ensure adequately high compound viscosities and the avoidance of sunlight-degraded rubbers. The deleterious effect of sunlight exposure of NR on tensile properties, resilience and heat build-up characteristics of vulcanisates has previously been demonstrated (O'CONNELL, 1966).

CONCLUSIONS

Phosphoric acid treatment, which is estimated to cost between 0.05 and 0.2 Malaysian cents per lb of rubber, can significantly improve the quality of certain types of raw natural rubber in respect of increasing the PRI and improving the ageing properties of gum vulcanisates with or without anti-oxidants present in the compound.

By increasing the PRI, sunlight-aged material can more reliably be avoided and the uniformity of the production is considerably improved. This increases its acceptability to the rubber manufacturer who is vitally concerned in having natural rubber with constant mastication and mixing characteristics without the necessity of selection and blending.

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DISCUSSION

Chairman: Dr. Sekaran Nair

Mr. M.G. Smith compared the addition of conventional phenol and amine anti-oxidants to raw rubber, which did not affect PRI values significantly, with their inclusion in ACS 1 compounds and the resultant improvement in ageing performance of the vulcanisate. Dr. Watson replied that natural rubber normally contained both anti-oxidants and metal-chelating agents. The presence or absence of chelating agents had a dominant effect on the PRI value because the test was carried out at 140°C. The loss of chelating agents seemed to be associated with the loss of anti-oxidants; the latter, being of the simple amine and phenol type, decomposed above 120°C and therefore did not affect the PRI value.

Mr. P. van Gelder asked why the PRI as well as the initial plasticity of the rubber was lowered by exposure to sunlight. Dr. Watson suggested that these were due respectively to two effects of sunlight: formation of hydroperoxide groups initiating heat breakdown, and reduction of the molecular weight. Mr. J. O'Connell said chain branching may also occur on exposure to sunlight. Dr. Watson agreed, adding that branching may occur also on subsequent high temperature mastication of rubber exposed to sunlight.

Mr. H.N. Bien asked if the initial plasticity values of the rubbers had varied in the comparisons of the vulcanisate ageing properties of rubbers with different PRI. Dr. Watson said that there was some variation in initial plasticity but the compound viscosities had been equated in preparing vulcanisates so that the comparison of properties before and after ageing was valid.

Dr. C.H. Tan asked if the beta-carotene in natural rubber could act as a free radical initiator in oxidation. Dr. Watson said this and other non-rubbers might affect oxidation; these had not yet been investigated, but might repay study.

Dr. B.L. Archer suggested that the fall in PRI of raw rubber soaked in water might be due to the leaching of ascorbic acid which was very soluble in water. Dr. Watson replied that it was premature to attach significance to any one of the many natural anti-oxidants; moreover, the mechanism seemed complex because the fall in PRI was often sudden after an unpredictable period of ageing.

Mr. C.W. Thompson asked if oxalic acid treatment of rubber could be detected since PRI might become a specification test. Dr. Watson said a method could be developed if necessary, but he questioned the need, because phosphoric acid treatment did not cost as much.